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Advanced Methodologies for Sampling and Analysis of Toxic Organic Chemicals in Ambient Outdoor, Indoor, and Personal Respiratory Air

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16. ABSTRACT

Many different kinds of sampling devices and analytical techniques are required to assess the potential adverse effects of toxic air pollutants on human health and the ecosystem. The U.S. Environmental Protection Agency has an on-going research and development program designed to provide the necessary tools to monitor air quality both outdoors and indoors and to measure personal respiratory exposures. Particular emphasis in recent years has been placed on real-time and integrative methods for neutral and polar volatile organic chemicals (e.g., chlorinated hydrocarbons, single-ring aromatics, alcohols, aldehydes, ethers, thiols, nitriles) and semivolatile organics (e.g., polynuclear aromatics, nitrated aromatics, pesticides, phenols). Samplers capable of obtaining sufficient quantities of chemicals for ultratrace analyses and sometimes bioassay, that are also quiet, unobtrusive and user-friendly, are being developed and evaluated for indoor, outdoor, and personal monitoring. New analytical techniques such as matrix-isolation GC/FTIR, and supercritical fluid extraction and chromatography are being adapted to characterize collected samples.

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Invited Paper

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ROBERT G. LEWIS

Atmospheric Research and Exposure Assessment Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711 (USA)

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Many different kinds of sampling devices and analytical techniques are required to assess the potential adverse effects of toxic air pollutants on human health and the ecosystem. The U.S. Environmental Protection Agency has an on-going research and development program designed to provide the necessary tools to monitor air quality both outdoors and indoors and to measure personal respiratory exposures. Particular emphasis in recent years has been placed on real-time and integrative methods for neutral and polar volatile organic chemicals (*e.g.*, chlorinated hydrocarbons, single-ring aromatics, alcohols, aldehydes, ethers, thiols, nitriles) and semi-volatile organics (*e.g.*, polynuclear aromatics, nitrated aromatics, pesticides, phenols). Samplers capable of obtaining sufficient quantities of chemicals for ultratrace analyses and sometimes bioassay, that are also quiet, unobtrusive and user-friendly, are being developed and evaluated for indoor, outdoor, and personal monitoring. New analytical techniques such as matrix-isolation GC/FTIR, and supercritical fluid extraction and chromatography are being adapted to characterize collected samples.

INTRODUCTION

Early efforts to develop methods for the determination of air pollutants were largely in response to the needs of industrial hygiene. Usually only one compound was measured and targeted air concentrations were normally in the milligram-per-cubic-meter (ppm) range; therefore, sampling for short periods (10 min to several hours) at low flow rates (0.1 to 10 L/min) provided adequate samples for analysis even before the advent of highly sensitive analytical methodologies. Bubblers, gas scrubbers, and liquid impingers were most often used, although small columns of solid sorbents and filters were sometimes employed. While such methods are often still appropriate for occupational health monitoring, they are inadequate for assessing the quality of the air breathed by the average person or for monitoring atmospheric pollutants that are important from the standpoint of global contamination. Microgram-, nanogram- and sometimes picogram-per-cubic meter (ppb to ppq) concentrations of air pollutants of diverse chemical classes and physical states are presently of concern in many countries.

Serious efforts to deal with the problems associated with air pollution in the United States began with the passage of the Clean Air Act in 1963. The creation of the U.S. Environmental Protection Agency (U.S. EPA) in 1970, subsequent amendments to the Clean Air Act, and the Radon Gas and Indoor Air Quality Act of 1986 provided the impetus and funding for research programs to develop the monitoring methods needed to evaluate air quality. While much progress has been made, adequate monitoring methods for many air contaminants of concern are still lacking. Methods that are suitable for outdoor use may not be useful indoors because the samplers are too large or too noisy. Still smaller, less obtrusive samplers are required for personal monitoring. In this paper, we will discuss recent progress in measuring organic chemicals in outdoor, indoor and respiratory air.

DISCUSSION

Organic chemicals can be categorized by volatility into three groups: *volatile*, *semivolatile* and *nonvolatile*. The ranges of vapor pressures associated with these categories are $> 10^{-2}$, 10^{-2} to 10^{-8} kPa, respectively[1]. Volatile organic chemicals (VOCs) are generally present in the atmosphere in the gaseous state only, and many are found in urban outdoor air at concentrations in the 0.1 to 10 $\mu g/m^3$ range. Indoor air in residences, offices, public access buildings and transportation vehicles often contains VOCs at levels an order of magnitude higher than outdoors. Semivolatile organic chemicals (SVOCs) are usually in the ambient outdoor air at pg/m^3 to ng/m^3 concentrations, but may be present at high ng/m^3 to $\mu g/m^3$ levels indoors. These chemicals may exist distributed between the vapor and particle-associated phases, making air sampling more complicated. Nonvolatile organic chemicals (NVOCs) are entirely particle-associated and generally found at still lower concentrations in air. Some typical chemicals of each type are shown in Table I.

Many organic chemicals are polar and present special problems in sampling and analysis. Polar organic compounds may be categorized as either ionizable or polarizable. The former category includes alcohols, phenols, amines, and organic acids; the latter group includes ketones, ethers, nitro compounds, nitriles, and isocyanates. Polar derivatives of organic compounds are often more toxic than the parent compounds, especially in the case of polynuclear aromatic hydrocarbons (PAHs). It is believed that oxy- and nitro-PAHs may account for

Table Ia Vapor Pressures of Some Volatile Organic Compounds at 25°C

Vapor Pressure, kPa	Chemical Class			
	Chlorinated	Oxygenated or Nitrogenous	Normal Alkanes	Aromatic
	Methyl Chloride Vinyl Chloride	Dimethylamine Phosgene Ethylene oxide	Butane	
100				
	Dichloromethane Chloroform Carbon Tetrachloride	Acrolein Acetone Acrylonitrile Methanol	Pentane Hexane	Benzene
10				
	Tetrachloroethylene Chlorobenzene	1,4-Dioxane	Heptane Octane	Toluene Xylenes
1				
	Monochlorotoluenes	Methylmeth-acrylate Benzaldehyde	Decane	Styrene Mesitylenes
10^{-1}				
	p-Dichlorobenzene Hexachlorobutadiene	Toluene-2,4-diisocyanate Aniline Toxaphene Phenol	Dodecane	
10^{-2}				

Table Ib Vapor Pressures of Some Semivolatile Organic Compounds at 25°C

Vapor Pressure, kPa	Chemical Class			
	Chlorinated	Oxygenated or Nitrogenous	Normal Alkanes	Aromatic
	Tetrachlorobenzenes 2,4,5-Trichlorophenol Dichlorvos	Nicotine *p*-Chloroaniline *p*-cresol	Tetradecane	Naphthalene Biphenyl
10^{-3}				
	Pentachlorobenzene	*p*-Nitroaniline	Hexadecane	Anthracene
10^{-4}				
	Aroclor 1242 Pentachlorophenol Heptachlor	Diazinon Dibutylphthalate	Octadecane	Phenanthrene
10^{-5}				
	Hexachlorobenzene Chlordane Aroclor 1260	Parathion Carbaryl Stearic Acid	Eicosane	
10^{-6}				
	Dieldrin 2,3,7,8-Tetrachloro-dibenzo-*p*-dioxin	Anthraquinone	Hexacosane	Fluoranthene
10^{-7}				
	DDT	Di(2-ethylhexyl)phthalate		Benz(a)anthracene
10^{-8}				

Table Ic Vapor Pressures of Some Nonvolatile Organic Compounds at 25°C

Vapor Pressure, kPa	Chemical Class			
	Chlorinated	Oxygenated or Nitrogenous	Normal Alkanes	Aromatic
			Nonacosane	Chrysene
10^{-9}				
				Benzo(a)pyrene
10^{-10}				
				Benzo(ghi)perylene
10^{-11}				
10^{-12}				
				Coronene
10^{-13}				

a major part of the mutagenicity of airborne particulate matter. The state of monitoring methodology of polar organic chemicals is far behind that for nonpolar chemicals.

Volatile Organic Chemicals

Until recently, the most useful method for collecting VOCs from air was by accumulation on a solid sorbent. Typically, 2 to 100 L of air are pumped through a sorbent bed containing 0.1 to 2 g of sorbent. While popular for occupational exposure monitoring, activated charcoal has not seen much use as a sorbent for ambient air monitoring since it requires extraction with carbon disulfide or other polar solvents for recovery of most analytes and because it readily absorbs water from the air. When detection limits in the sub-ppb range are required, sorbent desorption cannot generally be used. Thermal desorption, by which the total quantities of analytes collected can potentially be transferred from the sorbent to the analytical device, is ineffective at removing all but the most volatile compounds from charcoal. The porous polymeric resin Tenax® (2,4-diphenyl-*p*-phenylene oxide), which is stable to about 300°C, may be thermally desorbed and has low affinity for water. Consequently, it has enjoyed wide-spread use for ambient air monitoring.

Unfortunately, there are many problems associated with sampling on Tenax®. One of these is break-through of the more volatile compounds, such as monochloroethylene (vinyl chloride) and dichloromethane. Polar VOCs are also poorly retained by Tenax®. Contamination, interferences and artifact formation are also particularly troublesome problems. Benzene, benzaldehyde, acetophenone and other compounds may be produced from thermal breakdown of the polymer during desorption and reactions may occur between co-collected analytes before and especially during desorption[2]. To validate the results of Tenax® sampling, the U.S. EPA proposed a technique called distributed air volume (DAV) sampling[3], which is based on the assumption that the amount of collected analyte should be a linear function of the volume of air sampled. The technique calls for simultaneous sampling through four tubes containing 1.2 g each of Tenax®-GC at widely different flow rates. Thus, four different volumes (*e.g.*, 5, 10, 20 and 40 L) of the same air parcel are collected. If the concentration of the analyte is independent of sample volume, the results are presumed to be accurate. If the concentration of analyte is not constant within analytical error across the set, break-through, artifact formation, or other complications have occurred and the sample is invalidated.

Carbonaceous polymeric sorbents (*e.g.*, Ambersorb® and Carbosieve®), which have come onto the market in recent years, have high retentions of volatile and polar compounds, but they also collect water and retain the less volatile VOCs too well for quantitative thermal desorption. Attempts at minimizing the various problems associated with sorbent sampling for VOCs has been made by combining Tenax®, carbonaceous sorbent, and charcoal beds into one tube[4]. While this approach eliminates most breakthrough problems and minimizes moisture collection, thermolysis and other reactions may create artifacts. In addition, thermal desorption allows only one analysis per sample.

One technique that is essentially free of artifact problems was recently developed by the U.S. EPA[5,6]. The method employs whole-air collection in evacuated stainless-steel canisters, the interiors of which have been passivated by an electropolishing procedure known as SUMMA®-polishing. Air may be sampled into these canisters at controlled flow rates either by use of a critical orifice or mass-flow controller without the aid of a pump, or a pump may be used to fill the canisters to pressures up to several atmospheres. An aliquot (250 to 500 cm^3) of the canister contents is cryofocused into a gas chromatograph for analysis with a mass selective detector (MSD) or traditional GC detector. Detection limits are generally below 1 $\mu g/m^3$ when an MSD is used,

and may be much lower for certain VOCs when other detectors are used. A distinct advantage over thermally-desorbed sorbent sampling is the ability to perform repeated analyses on the same or different analytical systems. Nonpolar VOCs with vapor pressures as low as 10^{-2} kPa and polar VOCs as reactive as ethylene oxide have been shown to be stable inside these canisters for periods of one to several weeks. However, when MSD analysis is performed, the sample aliquot is normally passed through a perfluorinated ionomer membrane (Nafion® tubing) to remove co-collected water. This process also effectively removes many of the polar VOCs. Chemical ionization MS using water vapor or other chemicals as the reagent gas is currently under investigation to permit *in situ* analysis of polar VOCs with the ion trap detector.

In one sampler design used successfully by the U.S.EPA, 6-L canisters are filled passively by means of mass-flow controllers. At 3 to 4 cm^3/min, *ca.* 5.5 L of air can be collected over a 24-h period. A timer and solenoid-controlled valving system has also been designed to permit intermittent sampling with this system for periods up to one week[6]. With pump-driven samplers, *ca.* 14 L of air can be sampled into the 6 L canister at 11 cm^3/min over 24 h. Several U.S. manufacturers have recently introduced this type of sampler based on U.S.EPA designs. Some of these are compact (*e.g.*, 30 x 56 x 48 cm, 23 kg) and are very quiet in operation, making them well suited for indoor sampling. Since they are also weatherized, the same samplers may be used outside.

A variation of the canister sampler is a 12-syringe sampler designed by the U.S.EPA in cooperation with its manufacturer (SIS, Inc., Moscow, Idaho). It is portable, battery-operated, and can be programmed to consecutively fill the SUMMA®-polished syringes (150 cm^3 each) at rates ranging from 2 to 90 min per syringe[7]. Analysis by GC/MSD is fully automated to analyze sequentially the contents of each syringe with a detection limit of less than 1 $\mu g/m^3$ for most VOCs. The sampler has been used to determine temporal profiles of VOCs outdoors, in buildings and in motor vehicles.

With recent instrumental developments, VOCs may also be determined at ambient levels in real-time or near-real-time. A U.S.EPA van-based gas chromatographic (GC) system[8] capable of automated continuous sampling and cryogenic collection is shown in Figure 1. In the sampling mode, air is drawn through the manifold at 40 L/min and a portion is sampled at *ca.* 35 cm^3/min through a Perma-Pure® dryer containing Nafion® tubing to remove water and into an automated cold trap at −170°C to collect nonpolar VOCs. At the end of the sampling period (up to 50 min out of every hour), sampling is suspended, the trap is rapidly heated to 150°C, and the trapped VOCs are purged into the GC for analysis. The trap is then rapidly recooled to resume sampling while the analysis is carried out (cycle time *ca.* 10 min). Reference gas mixtures containing up to 40 VOCs are periodically drawn into the analytical system for calibration.

The U.S.EPA has also conducted studies that have aided in the development of improved designs for portable GCs capable of semi-real-time ambient air monitoring[9]. One such system is the new Photovac® 10S70. The battery-operated GC, which measures 46 x 6 x 13 cm and weighs 13 kg, utilizes a photoionization detector (PID) and can determine up to 25 compounds simultaneously. The GC oven is isothermal at 50°C. Detection limits range from 0.1 to several ppbv for substituted benzenes and haloethylenes. However, sensitivity for saturated haloalkanes is poor (ppmv range). Another portable GC, the Scentograph® PC, provides better specificity through the use of argon ionization or electron capture detection and column temperature programmability. Its sensitivity is in the low ppbv range, generally poorer than that of the Photovac except for saturated compounds. It is also battery-operated and measures 48 x 57 x 18 cm; weight 18 kg.

Despite problems associated with sorbent

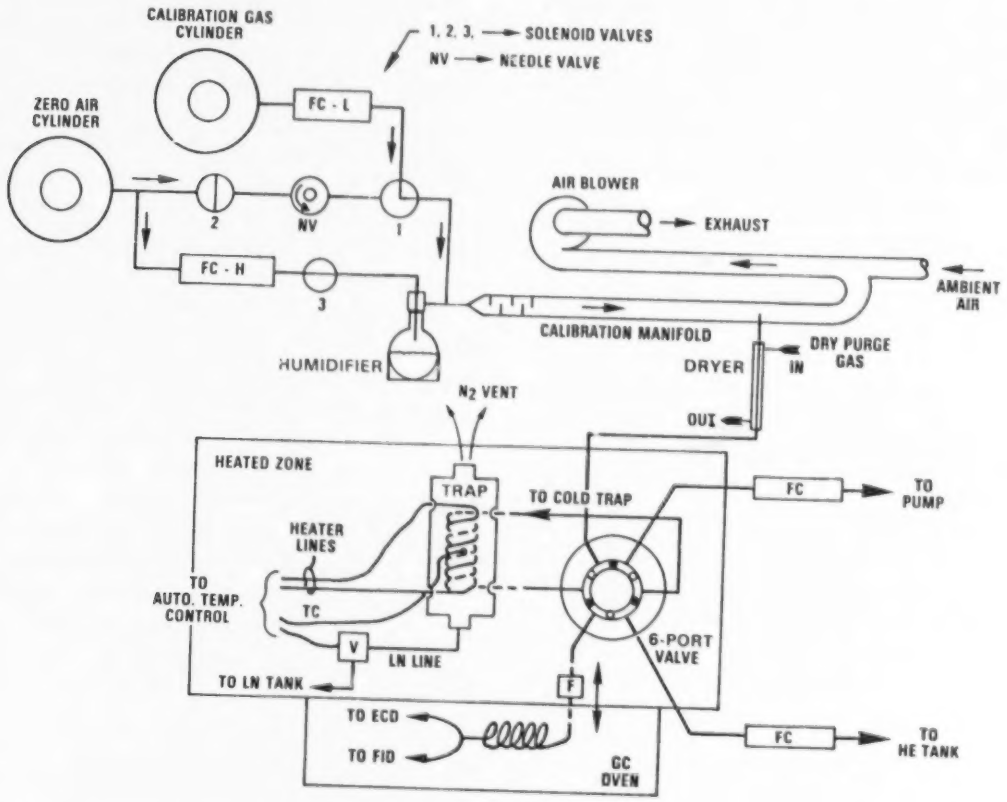

Fig. 1 Schematic diagram of automated continuous sampling and analysis system for volatile organic chemicals. FC-L and FC-H denote low-rate and high-rate flow controllers, respectively; T, LN, V and F denote thermocouple, liquid nitrogen, valves, oven connection, respectively.

sampling for VOCs, personal respiratory exposure monitoring requires sampling devices that are too small to be based on other techniques. Most U.S.EPA total human exposure studies have utilized small, battery-operated pumps and shielded glass sampling tubes containing 1.5 g of Tenax®[10]. Participants generally wore a vest with pockets to hold the sampler, which could operate at 30 cm^3/min for 12 h. The monitor has been successfully used to obtain several thousand measurements of personal and indoor air exposures, and has conclusively demonstrated that indoor air exposures exceed outdoor exposures by at least an order of magnitude for most VOCs[11]. In an effort to reduce the obtrusiveness of the monitor, a passive (diffusion-controlled) sampling device (PSD) was developed[12]. The PSD, shown in Figure 2, is a stainless steel cylinder (3.8 cm o.d. x 1.2 cm), which weighs 36 g and contains a small bed of Tenax® (0.4 g) or other sorbent. The device is thermally desorbable and has very high efficiency. Effective sampling rates of 75 to 100 cm^3/min for most VOCs permit detection limits of

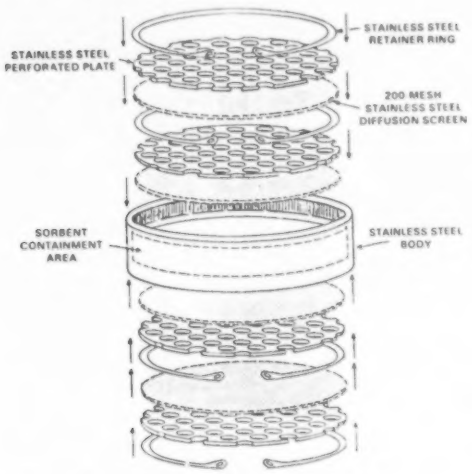
STAINLESS STEEL RETAINER RING
STAINLESS STEEL PERFORATED PLATE
200 MESH STAINLESS STEEL DIFFUSION SCREEN
SORBENT CONTAINMENT AREA
STAINLESS STEEL BODY

Fig. 2 High-efficiency passive sampling device.

1 ppbv or less with exposure times of 1 to 3 h. Problems due to reversible sorption, which is analogous to break-through in active samplers, arise at loadings above 1 μg of VOC (usually after several hours exposure for the more volatile VOCs). Mathematical corrections can be applied if break-through volumes are known, however. The PSD has been modified to reduce the effective sampling rate by a factor of 20 to 25 to permit 24-h exposure for nearly all VOCs[13]. The high-rate PSD is available from Scientific Instruments Specialists, Inc. as the SIS Passive Sampler (see Figure 3). The same company is currently developing a low-rate PSD that will be an improvement of the EPA design.

The PSD shown in Figure 2 has also been adapted for reactive sampling. For example, when

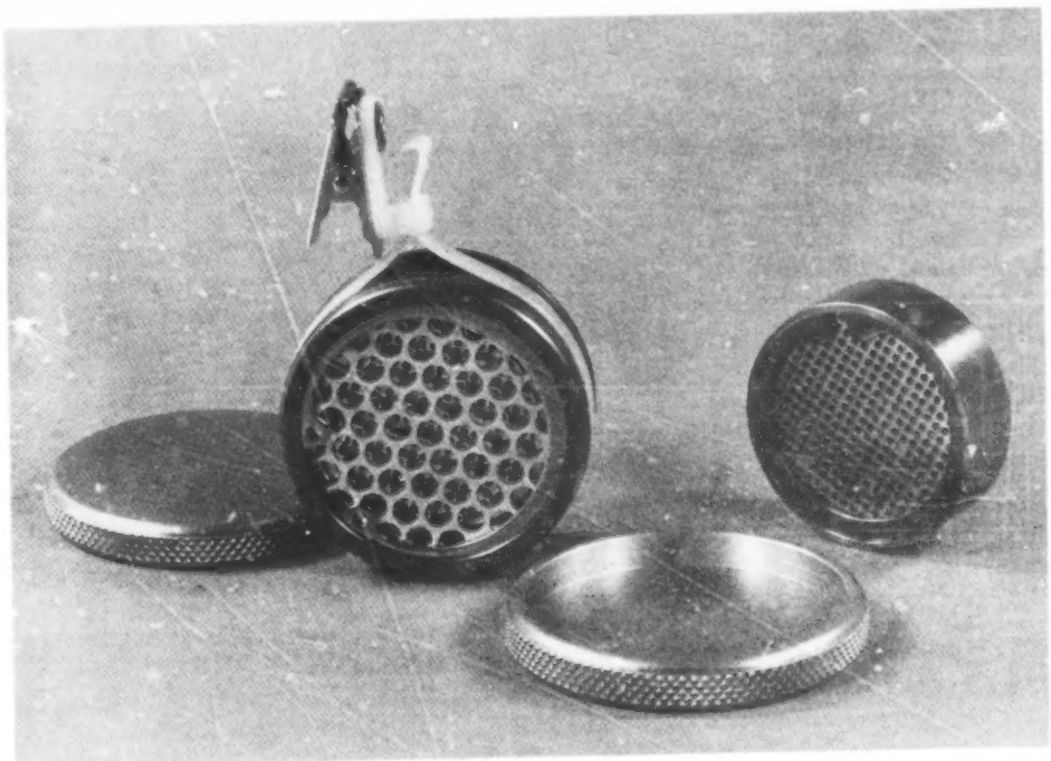

Fig. 3 Passive sampling device and protective cage.

the Tenax® sorbent bed is replaced with glass-fiber filters coated with 2,4-dinitrophenylhydrazine, aldehydes may be determined[14]. The sampling rate of this PAD for formaldehyde is 103 cm^3/min, or about 100 times faster than that of the standard Palmes tube. No capacity problems have been noted when analytes are collected on reactive media.

Most of the artifact problems (other than breakthrough) associated with Tenax® sampling are believed to arise from thermal reactions during desorption. U.S.EPA supported efforts are currently underway, therefore, to develop on-line supercritical fluid extraction (SFE) techniques for both pumped tubes and PSDs[15]. While it is easier to interface SFE with super-critical fluid chromatography (SFC), gas chromatography provides a more practical analytical finish. The SFE/GC system shown in Figure 4 permits on-line extraction and cryogenic preconcentration in *ca.* 30 min, followed by traditional gas chromatography. Analytical sensitivity is equivalent to thermal desorption at 250°C, but at temperatures of 35° to 50°C, analyte reaction potential is greatly reduced. In addition, low volatility compounds are also efficiently desorbed.

Semivolatile and Nonvolatile Organic Compounds

In numbers of different compounds, far more SVOCs and NVOCs than VOCs may exist in the atmosphere, although air concentrations are generally much lower. Polynuclear aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) are SVOCs that have been considered most important among air pollutants. Many of these SVOCs have vapor pressures that allow them to exist in the atmosphere distributed between the gaseous and particle-associated phases, and the equilibrium between phases will vary with ambient temperature, concentrations, particle size and type, and other atmospheric parameters[16]. When contaminated particles are entrained into the atmosphere, partitioning of the SVOCs into the gas phase will likely commence by vaporization. The extent of loss of a given SVOC from the suspended particles in transit from a source to a sampler placement site will depend on its vapor pressure, on the distance traveled, air temperature, and to a lesser degree on humidity, wind velocity, and particle size. Once collected onto a filter, volatilization may occur at an accelerated rate, making it impossible to obtain accurate measurements of organic particulate loadings by filtration sampling. In fact, nearly quantitative evaporation losses of pesticides having vapor pressures as low as 10^{-8} kPa have been observed from airborne particulate matter collected on glass-fiber filters[17]. Consequently, efficient collection of most SVOCs requires a sampler equipped with a particle filter in series with a vapor trap or a sorbent trap capable of retaining both particles and gases.

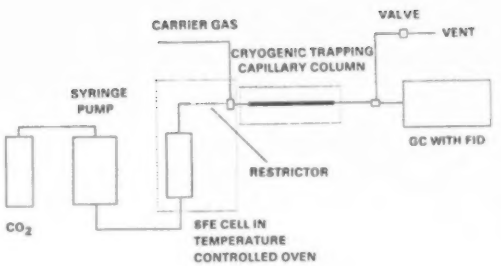

Fig. 4 On-line supercritical fluid extraction/gas chromatographic analysis system for air sampling devices.

A high-volume sampler capable of collecting SVOCs in both phases was developed by U.S.EPA in the early 1980s[18] and is commercially produced in the USA by General Metal Works, Village of Cleves, Ohio. The sampler draws air at flowrates up to 280 L/min through a 10-cm dia particle filter and a backup sorbent bed contained in a 6-cm dia x 13-cm glass cylinder (see Figure 5). The sorbent cylinder is designed for placement in a Soxhlet extractor so that granular sorbents may be extracted without unloading the trap. Flow rates of up to 225 L/min

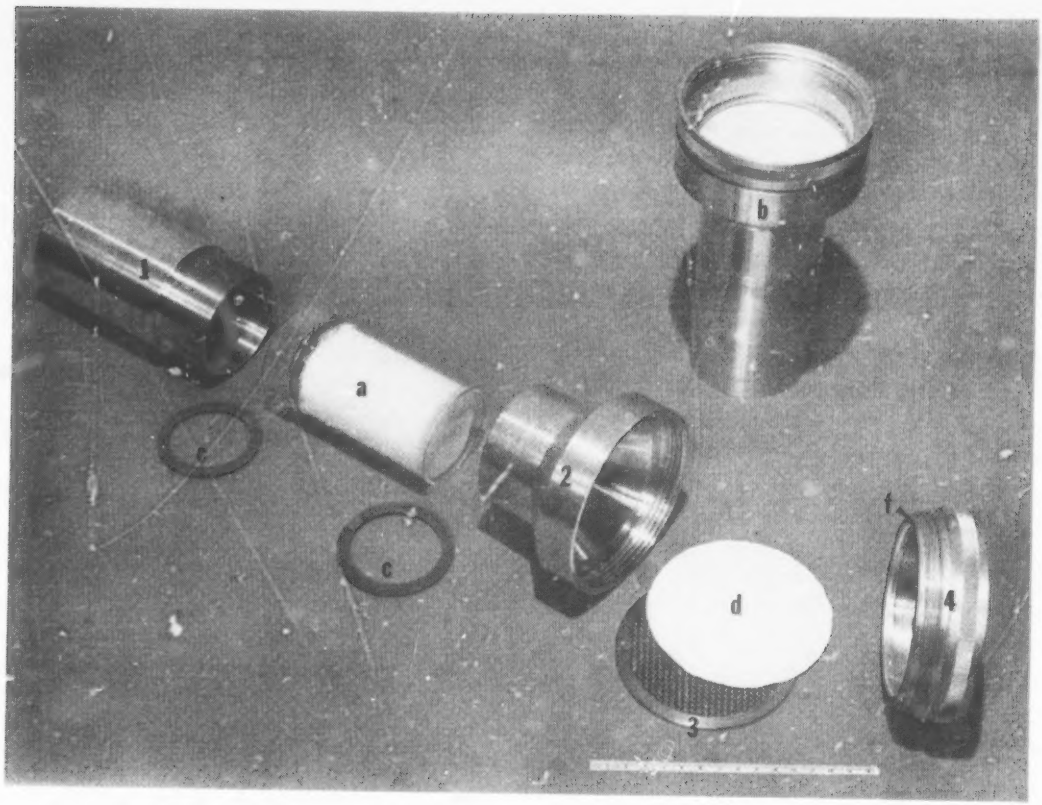

Fig. 5 High-volume sampling module for semi- and nonvolatile organic chemicals: (a) sampling cartridge; (b) assembled module containing cartridge and particle filter; (c) silicone rubber gaskets; (d) particle filter; (e) support screen; and (f) silicone rubber "O"-ring; part 1, cartridge receptacle; part 2, prefilter adapter; part 3, filter support screen; part 4, filter retaining ring.

can be maintained through bed depths of 5 cm of 16-to 20-mesh Amberlite® XAD-2 (weight 65 g) and similar macroreticular polymeric resins. Polyurethane foam (PUF), which has much lower density, offers substantially lower resistance to air flow and will permit higher sampling rates. Since it is also inexpensive and easy to use, it has become the most popular sorbent in the U.S. for collecting pesticides, PCBs, PCDDs, and PAHs from air. Compounds with vapor pressures greater than 10^{-3} or 10^{-4} kPa (depending on polarity) are not as efficiently trapped by PUF as by most granular sorbents. Combinations of PUF and a granular sorbent (*e.g.* by "sandwiching" 25 cm^3 of sorbent between 5-cm and 2.5-cm PUF plugs) will permit efficient trapping of most SVOCs at 250 L/min with minimal pressure drop[18]. The "sandwich" trap, or one containing XAD-2, is preferable to PUF alone for PAH sampling because 2- and 3-ring compounds can be efficiently trapped.

Since traditional sampling methods may greatly perturb the phase distributions of SVOCs during collection, filter and backup vapor traps should be extracted or analyzed together. Separate analyses may lead to incorrect conclusions concerning at-

mospheric phase distributions as well as underestimation of concentrations for compounds that are present in below-detectable amounts on either the filter or vapor trap (or possibly both).

Knowledge of phase distributions may be important for consideration of human health risk assessment. Therefore, the U.S.EPA has recently begun to investigate means of determining these distributions in air. A research-level sampling system based on denuder separation principles was designed to fit the SVOC sampler previously described[19]. The denuder assembly consisted of an array of seven 1.5-cm dia x 61-cm open tubes coated with Dow Corning® high vacuum silicone grease. The assembly and sampling module are shown in Figure 6. At a flow rate of 15 L/min, the denuder was 90% efficient at removal of naphthalene vapor and permitted particles down to 0.1 μm mean dia or less to quantitatively pass through to the filter. Studies conducted with this sampler showed that 3- and 4-ring PAHs exist to a large extent in the vapor phase in ambient air and that substantial losses of the compounds from the particle-absorbed phase can occur after collection on filters. Table II shows the medians and ranges of absorptions made during summer and winter months for PAH's with three or more rings. While 85% to 95% of the first four compounds were found in the PUF vapor trap, the results of the denuder sampling indicated that median proportions in the vapor phase prior to sampling were only in the 40 to 70% range. These compounds have vapor pressures ranging from 10^{-4} to 10^{-7} kPa. No vapor component was detected for any compound with a vapor pressure less that of chrysene (10^{-9} kPa). As expected, distributions were shifted toward the vapor state during summer months. Likewise, volatilization artifacts were larger during warmer weather.

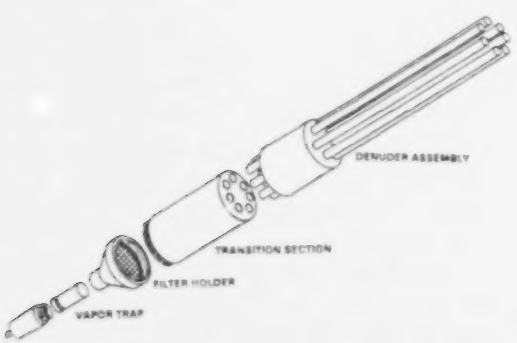

Fig. 6 Open-tube denuder assembly for determining phase distribution.

Table II Phase Distributions and Volatilization Artifact Levels of Polynuclear Aromatic Hydrocarbons[a]

COMPOUND	Percent in Vapor Phase Before Collection		Volatilization Artifact as Percent of Total	
	Median	Range	Median	Range
Antiuracene	57	14–92	32	13–92
Phenanthrene	51	25–86	45	13–80
Pyrene	43	5–80	47	16–83
Fluoranthene	43	27–64	43	7–62
Benz(a)anthracene	32	8–67	30	8–53
Chrysene	40	15–65	18	6–50
Benzo(a)pyrene	ND[b]		ND	
Benzo(e)pyrene	ND		ND	
Benzofluoranthene	ND		ND	
Perylene	ND		ND	
Benzo(g,h,i)perylene	ND		ND	
Indeno(1,2,3-c,d)pyrene	ND		ND	
Coronene	ND		ND	

a. Median and ranges of measurements made during summer and winter months.
b. ND = not detected.

The dependence of the distribution of PAHs between the vapor and particulate phases is well represented by the Dubinin-Radushevich isotherm:

$$\ln (W/Wo) = B/b^2 \{RT \ln P/Po\}^2$$

where W is the absorbed phase loading, Wo is the capacity of the sorbent, B is a constant that is characteristic of the sorbent, b is a function of the polarizability of the sorbate, P is the vapor phase concentration, and Po is the equilibrium vapor concentration for the pure compound. The term in brackets is the

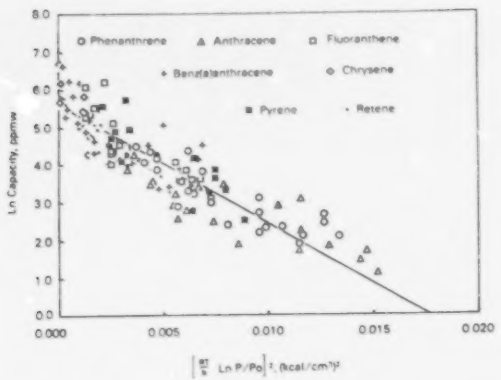

Fig. 7 Dubinin-Radushkevich plot for semivolatile polynuclear aromatic hydrocarbons.

isosteric heat of absorption which has units of energy/mole. This relationship is shown in Figure 7.

As a result of these investigations, and to meet the need to collect larger quantities of PAHs for improved analytical sensitivity, a high-volume compound annular denuder (HVCAD) has been developed[20]. The HVCAD, shown in Figure 8, is capable of efficient separation of vapors from particles at air flow rates of 200 L/min, providing sample sizes that are adequate for in-depth chemical analysis and bioassay for mutagenicity. Like the low-volume open-tube denuder, the HVCAD is designed to fit the PS-1 sampler, but is much smaller, measuring 8 cm dia x 20 cm. It is made up of twelve concentric cylindrical aluminum shells surrounding a solid aluminum core, with annular thicknesses of 1.6 mm. When the shells were coated with 30 μm-thick layers of silicone grease, the vapor collection efficiency (as measured with naphthalene) was >95% at 200 L/min with no detectable losses of particles down to 0.1 μm mean diameter. Recent field experiments with the HVCAD have yielded PAH phase distribution measurements similar to those shown in Table II.

It has not yet proved practical with either denuder to recover PAHs from the silicone grease-coated walls by solvent extraction or thermal desorption. Consequently, phase distributions must be determined by the "denuder difference" method. Collocated samplers, one with and one without a denuder, are operated simultaneously for a 24-h period. The total quantity (filter plus vapor trap) collected by the denuder sampler corresponds to the particle-associated phase and this is subtracted from the total quantity collected by the nondenuder sampler to estimate the vapor phase portion. The quantity recovered from the vapor trap of the denuder sampler is taken as the volatilization artifact. The rate of post-collection volatilization from the filter is potentially higher in the denuder sampler since the incoming air is free of PAH vapor. Nevertheless, the total vapor phase volatilization artifact values obtained by this method agrees well with the quantities of PAHs found in the vapor trap of the nondenuder sampler.

To study indoor air pollution by PAHs, U.S.EPA modified the PS-1 sampler by housing the pumping system in an acoustically-insulated cabinet[21]. This sampler is very quiet in operation and has been successfully used in several multi-home studies. It provides a sufficient sample volume in 12 to 24-h for in-depth GC/MS analysis as well as mutagenicity testing. However, it is large, and the flow rate is too high for use in smaller enclosed areas. Consequently, a lower flow sampler (15 to 20 L/min) has been designed with similar features[22]. Air is drawn through a 47-mm circular quartz-fiber filter and subsequently through a glass cartrid containing 60 g of Amberlite® XAD-2 resin. When evaluated for continuous 24-h periods (150 m^3 sample volume) and in an intermittent mode for 7 days (190 m^3 sample volume), the collection efficiency of the sampler is 90% or better for 29 PAHs with two to six rings. Detection limits using electron ionization GC/MS for nonpolar and negative chemical ionization GC/MS for nitro- and oxy-PAHs were 0.1 ng/m^3 or lower. When XAD-4 resin is used, nicotine is also efficiently collected[23]. A small compound annular

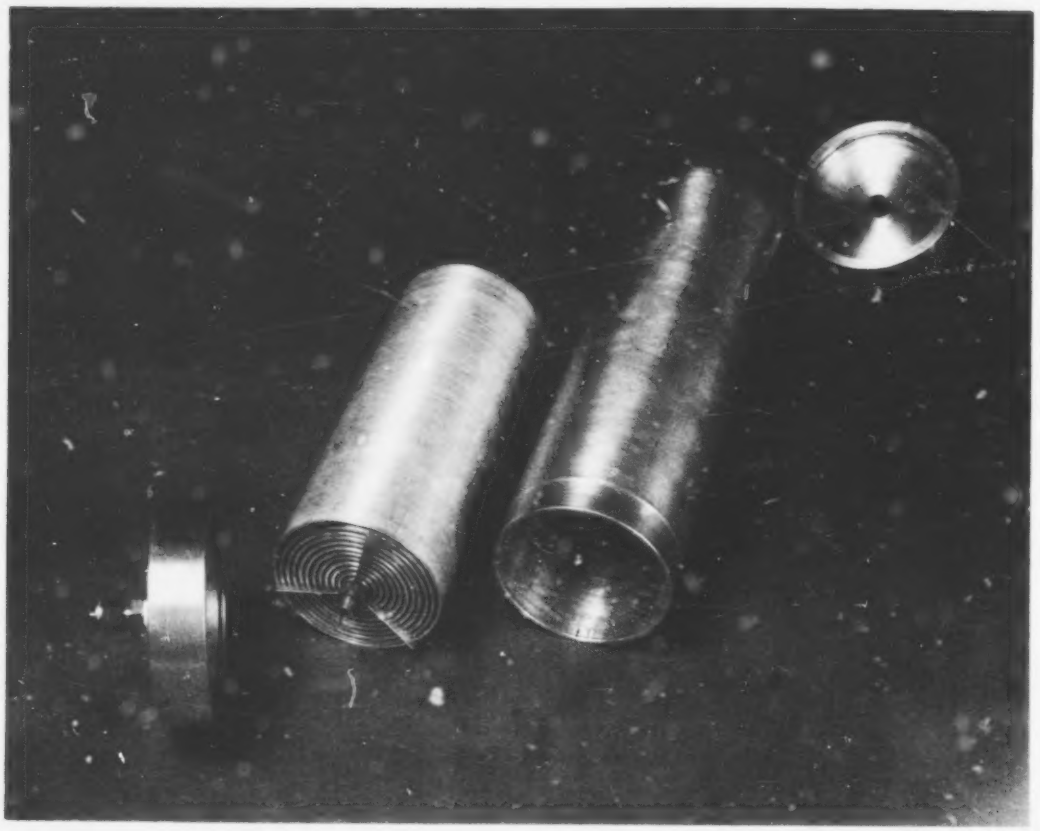

Fig. 8 High-volume compound annular denuder assembly with case and endcaps.

denuder has also been constructed for this sampler.

Pesticides[23], PCBs[23,24], PCDDs[25], and PCDFs[25], have been successfully determined in ambient air with the PS-1 sampler using PUF backup traps. These methods have been adopted as EPA Methods TO4 and TO9[26]. As in the case of pesticides, PCBs are collected almost entirely in the vapor trap. Tetrachloro isomers of PCDDs and PCDFs have been shown to volatilize quantitatively from particulate-loaded filters, while the octachloro isomers are mostly retained on the filters[25].

The methodology used most widely in the U.S. for monitoring pesticides in indoor air was developed by U.S.EPA in 1982[27]. It has recently been used in a large nonoccupational exposure study involving about 270 households to determine airborne concentrations of over 30 pesticides[28,29] and has been adopted in the U.S. by EPA as Method TO10[26], by ASTM as Standard Practice 04861[30], and WHO in Europe[31]. Small personal pumps are used to sample air at 3.8 L/min through a cylinder of polyurethane foam 22-mm o.d x 7.6-cm long. The 5.5 m^3 volume of air sampled in 24 h provides limits of detection ranging from 1 to 100 ng/m^3 depending on the compound and analytical finish (GC/MS or GC/ECD).

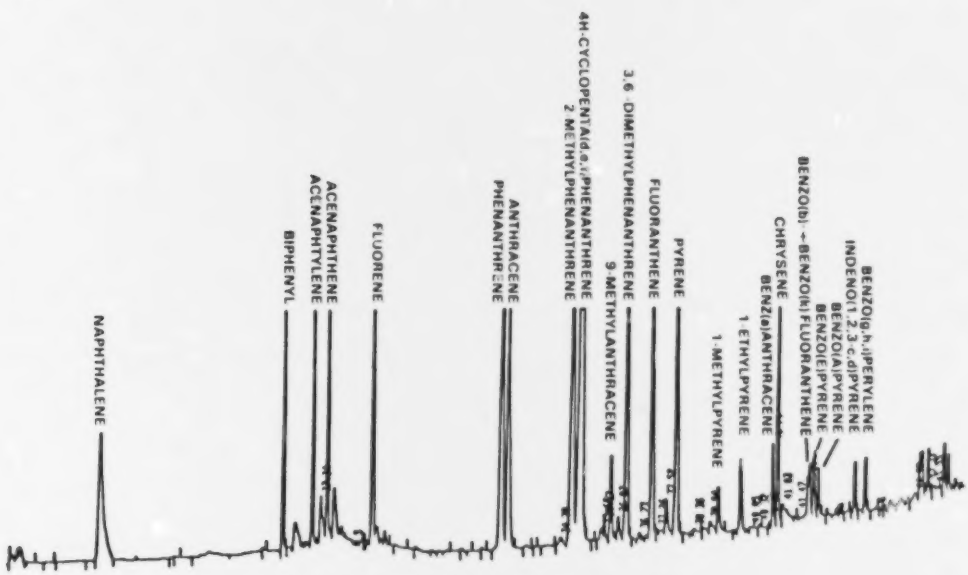

Fig. 9 Chromatogram of on-line SFE/GC analysis of polynuclear aromatic hydrocarbons.

The analytical determination of SVOCs and NVOCs is generally more difficult than for VOCs. They are generally present at low atmospheric concentrations, and are more difficult to isolate from sampling media.. Analyses of complex mixtures are often involved and high boiling points may complicate chromatographic separation. The sample preparation, which usually involves sorbent extraction from the sorbent or particle filter, may take up to 24 h. Even with extreme concentration (*e.g.* to 100 μ L), usually only a very small portion (*e.g.*, 0.2 to 5%) of the extract can be analyzed. Consequently, desired analytical limits of detection may not be achievable unless large air volumes are sampled.

On-line supercritical fluid extraction is a promising means of circumventing time-consuming and tedious sample preparation. Recent success has been obtained with on-line SFE/GC to analyze PAHs collected on XAD-2 resin in EPA-supported studies[15,32]. A typical chromatogram is shown in Figure 9. For polar, thermally labile and high-molecular weight organic compounds, SFE/SFC is more valuable, but relatively few SFC instruments are in use.

Whether GC, SFC, or high performance liquid chromatography (HPLC) is used for separation, mass spectrometry is generally the choice for analytical detection and measurement of SVOCs. However, for PAHS and some other classes of compounds, important isomers exist that cannot be easily separated. These isomers may differ greatly in toxicity and cannot be distinguished by their mass spectra. Infrared spectroscopy can readily discriminate between isomers, but its use in environmental analyses has historically been limited by its relatively poor sensitivity. Conventional coupling of GC to Fourier transform infrared (FTIR) spectrometers by means of optical light pipes has only been useful for determining VOCs when present in air samples in the high $\mu g/m^3$ concentration range (*e.g.*, near pollution sources). The recent development of on-

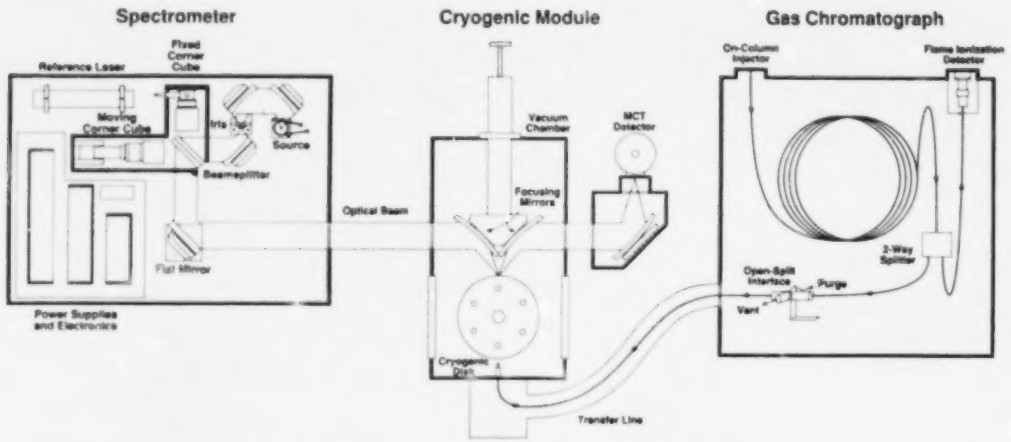

Fig. 10. Schematic diagram of the Mattson Instruments Cryolet® GC/MI-FTIR system.

line matrix isolation (MI) techniques has, for the first time, bought IR characterization into the arena of ultratrace analytical chemistry. This technique involves trapping analytes as they are eluted from the GC column in an inert matrix at cryogenic temperatures. In the Mattson Instruments (Madison, Wisconsin) cryolet instrument shown in Figure 10, the GC effluent is deposited on a rotaing, gold-plated disk where it is frozen at *ca.* 14°K in a matrix of argon (a component of the carrier gas). At the completion of chromatography, the disk (which is housed in a chamber evacuated at 10^{-7} kPa) is rotated in the opposite direction to bring specific elements into the IR beam for analysis. High sensitivities may be obtained since intermolecular interactions and molecular rotations are essentially eliminated by the isolation of each molecule of the analyte in a matrix of inert atoms at near absolute zero. In addition, they may be kept frozen on the disk indefinitely, permitting as many IR scans as desired. It is possible, therefore, to characterize analytes in the 100 pg range.

EPA has applied GC/MI-FTIR to the analysis of PAHs in ambient air samples[33,34]. Its utility in identifying coeluting PAH isomers in an extract of ambient air particulate matter is exemplified in Figure 11. Figure 11A shows a series of MI-FTIR spectra acquired at discrete time intervals across a GC peak centered at 41.28 min (peak width 0.60 min). It can be readily seen from comparison with the reference spectra presented in Figure 11B that three coeluting benzofluoroanthene isomers constituted the GC peak. These three isomers are indistinguishable by traditional GC/MS.

GC/MI-FTIR detection limits for unsubstituted PAHs are in the low ng range. For substituted PAHs, PCBs, PCDDs, and many other compounds that have strong IR-absorbing substituents, pg quantities can be detected. These detection limits approach those of GC/scanning electron-ionization MS. The quantitative capabilities of the technique have not yet been fully evaluted. The major disadvantages of the current technology are the lack of a comprehensive spectral library (*ca.* 12,000 spectra are available) and the significant time that is required for interpretation of results. The combination of GC/MI-FTIR and MS provides a powerful tool for determination of complex mixtures of organic chemicals.

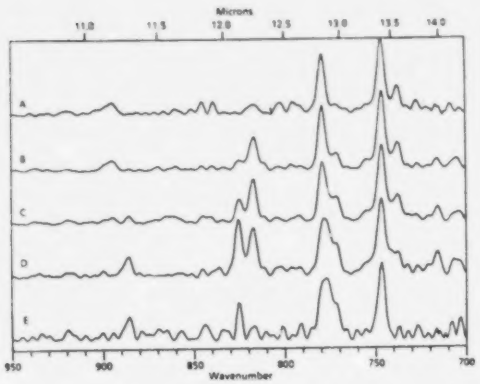

Fig. 11A Matrix-isolated infrared spectra of the components of an urban air particulate matter extract with a retention time of: (a) 41.04 min; (b) 41.16 min; (c) 41.28 min; (d) 41.46 min; and (e) 41.58 min.

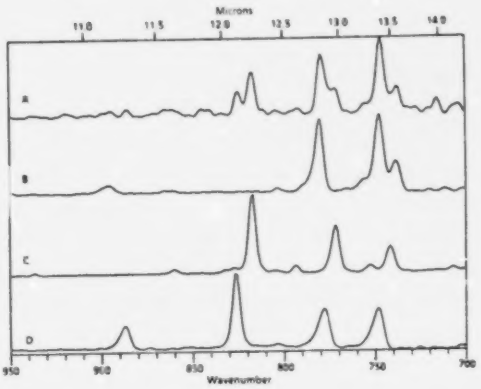

Fig. 11B Matrix-isolated infrared spectra of: (a) the component of the urban air particulate matter extract with a retention time of 41.28 min; (b) benzo[b] fluoranthene reference standard; (c) benzo[j] fluoranthene standard; and (d) benzo[k] fluoranthene reference standard.

CONCLUSION

Nearly a million synthetic organic chemicals have been catalogued and potentially millions more may exist. Animal toxicity tests suggest that many of these may be harmful to man. In fact, over 88,000 chemicals are listed in the Registry of Toxic Effects of Chemical Substances[35]. It has been estimated that at least 100,000 organic compounds can be expected to be present in a sample of air at a concentration level of one-part-pertrillion[36]. Specific air monitoring methodology exists for only a few of these, and multiresidue methods are capable of determining perhaps 100 to 200. (The U.S.EPA has published 14 methods for the determination of organics in ambient air[26]).

Currently, the U.S.EPA regulates no organic chemicals in ambient air and only two (benzene and vinyl chloride) in source-related air. However, a number of toxic organic chemicals are under Agency review for possible regulations and a recently-proposed amendment[37] to the Clean Air Act names 187 chemicals, mostly organic, that should be regulated. Methods do not exist for many of these compounds, particularly those that are polar. Consequently, a progressive research and development program must be strengthened to meet the emerging needs of the U.S.EPA and the world community. We must increase our understanding of the potential threat to human and ecological well-being posed by the presence of toxic organic chemicals in indoor and outdoor air.

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DISCLAIMER

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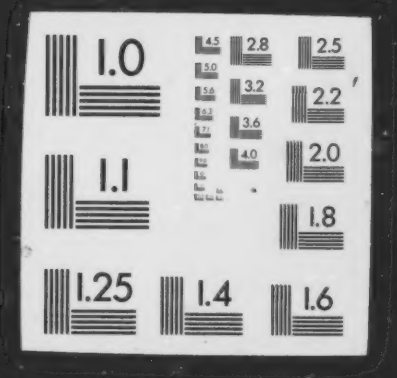

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Pesticide Sources to the Soil and Principles of Spray Physics

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16. ABSTRACT

In the past 50 years, organic pesticides have greatly enhanced the production and quality of food, feed, and fiber as well as the control of disease vectors and pests adversely affecting human health and welfare. In this review of the pesticides literature, the pesticide source term is characterized as it determines the primary and secondary pathways of transport to the soil surface. Factors influencing intra- and inter-compartmental transport are defined from a modeling perspective. Principles of spray physics are discussed, including the influence of application methodology, the influence of formulation on spray propagation, the effects of drift impingement to offsite areas, the metabolic efficacy of formualtions in killing pests. Also described are predictive models of the movement of sprayed pesticides.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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Chapter II

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In the past 50 years, organic pesticides have greatly enhanced the production and quality of food, feed, and fiber as well as the control of disease vectors and pests adversely affecting human health and welfare. Specifically, pesticides have been used in agriculture to increase productivity and the quality and quantity of food, feed, and fiber; in forestry for pest control in silviculture; in the industrial, commercial, municipal, and military sector for rodent and weed/brush control around plant sites and in right-of-ways; in medical vector control to reduce the numbers of mosquitoes, etc.; and in the urban environment for termite control in structures and pest control in gardens. For example, more than 500 different formulations of pesticides are usen in the urban environment and in excess of 11,363,636 kg (25 million pounds) of active ingredients are used in the gardens, yards and homes annually in the United States (USEPA, 1979). Agriculture represents the largest single market for pesticides.

The purpose of this chapter is to review the literature in order to (i) characterize the pesticide source term as it determines pesticide transport to the soil surface, which involves both primary and secondary pathways of transport to the soil; (ii) define factors influencing intra-and-intercompartmental transport; (iii) define the source term from a modeling perspective; (iv) discuss principles of spray physics (influence of application methodology, formulation on spray propagation, drift impingement to offsite areas, and metabolic efficacy in killing pest); and (v) describe predictive models of spray movement.

2-1 PESTICIDE ENTRY INTO THE ENVIRONMENT

Pesticides may be introduced directly into the environment in a liquid phase, as a dispersion or solution, or in the solid phase, as a powder, dust, microcapsule or granule. Sprays are directed to foliage or to the soil or are applied stoichastically to these same media as rainout (Fig. 2-1 and 2-2). Solids are applied directly to the soil surface, or to foliage. Pesticides also may be incorporated directly into the soil, usually in the top few mm to exert a biological effect. A pesticide also may enter the environment as a result of accidental spill or malicious application for waste disposal purposes.

Environmental entry and transport processes can occur either between or during a rainfall event. Those direct or primary transport processes to the soil surface that occur during a rainfall event include wet deposition and foliar washoff. Secondary transport processes to the soil surfaces that occur between rainfall events include spray drift and dry deposition. (The source term is particulates emanating from the pesticide drift process and pesticide found on dust particles generated by wind pickup and atmospheric transport.) Pesticides dissolved in atmospheric water vapor may be deposited either on the soil surface directly or indirectly to the foliar surface with subsequent removal during rainfall events via the process of foliar washoff. Therefore, pesticide sources to the soil surface include application events, atmospheric wet or dry deposition, foliar washoff, or accidental spills onto the soil surface or into the soil profile. Environmental sinks for pesticides include chemical, photochemical and biological transformation, volatilization losses, erosion and runoff; leaching; harvest removal and storage.

The mass balance is given by

$$\underline{\text{Pesticide Application}},\ \text{kg ha}^{-1} = \Sigma\ \underline{\text{Pesticide Sinks}}$$

[Chemical, photochemical, biological, and volatilization losses + Erosion + Runoff + Leaching + + Harvest + Storage (surface, upper and lower zone) (Bailey et al., 1985)]

Pesticides are applied directly to the soil as (i) preplanting treatments; (ii) pre-emergence treatments; (iii) postemergence treatments; or (iv) soil sterilants. Several factors influence the final concentration of soil-applied pesticide including: volatilization, photochemical degradation, chemical and biological transformation, leaching, and sorption. The initial pesticide source location, i.e., foliage or soil surface on day of application, depends upon the pest being controlled, pesticide concentration and formulation, and the mode of application. From a mass balance modeling standpoint, it is imperative to know at the time of application the pesticide concentration on the soil surface, plant canopy, or plant residue surface (or, if incorporated, the depth of incorporation). The knowledge of the initial concentration of pesticide in the applicator tank is not sufficient as up to 60 % of the applied tank concentration (Smith et al., 1976) may be lost through spray drift and volitilization. Secondary transport processes include foliar washoff, foliar drip (occurring on application day), rainout, and volatilization from foliar and soil surfaces. The concentration of pesticide available for transport is determined by the time-varying processes/sinks including biotic/abiotic transformation, volatilization, plant uptake, plant harvest (root and foliar absorption), leaching, and foliar residue washoff. These sources and major transport processes can be seen in Table 2-1. The

major pesticide sources for "offsite" transport include plant residue,soil surfaces, root or grain materials, foliage (for dissolved pesticide runoff), eroded soil particles (for sorbed pesticide), granules, dust or microcapsules, and leachates (for pesticide dissolved in solution or bound to colloidal particles).

2-2 PESTICIDE PROPERTIES

Traditionally in a presentation on pesticide properties, an extensive discussion would focus on the major families and classes of pesticides -- specifically their structures and their specific physical and chemical properties. However, because of a proliferation of classes of pesticides over the years, this is not practical for purposes of this review. The reader is referred to a variety of references on the structures and physical and chemical properties of specific pesticides -- insecticides (Brown, 1951; Metcalf, 1955; Kubr and Poogh, 1976), herbicides (Kearney and Kaufman, 1975, 1976; Klingman and Ashton, 1982; Weed Society of America, 1983), and fungicides (Torgeson, 1969; Luken, 1971; Marsh, 1972, Sharville, 1979).

Beacuse we are interested in pesticide source characterization -- transport, transformation, and behavior to, within, and from soil, insight into important chemical characteristics is imperative. Chemical characteristics that influence pesticide transport to and from soil include (i) ionic state (cationic, anionic, basic, or acidic); (ii) water solubility; (iii) vapor pressure; (iv) hydrophobic/hydrophilic character; (v) partition coefficient; and (vi) chemical, photochemical, and biological reactivity (Bailey et al., 1985).

Over the last 10 to 15 yrs, the general characteristics of pesticides have changed drastically. The use of extremely low water solubility, strongly sorbed (extremely hydrophobic and with a very high partition coefficient), and non-mobile formulations has changed to application of materials that are more water-soluable, only slightly sorbed (more hydrophilic and lower partition coefficient value - a K_d of 1 or less), and more mobile (Carsel and Smith, 1987). Part of this change is response to environmental problems (bioaccumulation and magnification) associated with earlier formulations and the increase pest resistance to chlorinated hydrocarbon pesticides.

Pesticide properties combined with the amount of pesticide applied and entering the environment determine how much pesticides can be transported along each route from source to receptor. (Specific routes can be seen in Fig. 2-1 and 2-2.) Possible intra-compartmental transport routes include foliar washoff to the soil surface, infiltration, percolation, and movement to lower storage zones and finally to ground water. Possible inter-compartmental transport routes include overland flow; interflow to subsurface water; and direct loss to the atmosphere from the soil, subsoil or foliar surfaces or losses due to movement of sediment-bound pesticide (both water and wind modes of transport) (Bailey et al., 1985).

Sorption processes determine the relative distribution among the vapor phase, the solution phase, and the surfae-bound phase; this distribution dictates the primary or secondary transport routes.

Environmental persistence in the soil is related to the individual pesticide's properties. A persistent compound dose not hydrolyze or biodegrade readily (first-order transformation rate constant is < 0.02 day^{-1}), has a loe volatilization or Henry's law constant, has a high partition coefficient and

has a high potential to move to and contaminate ground water (Carsel and Smith, 1987). A nonpersistent pesticide hydrolyzes and/or biodegrades readily (first-order degradation rate in soils at least 0.02 $days^{-1}$), has a low Henry's law constant, is highly water-soluble, (partition coefficient $K_d < 1$), and has an appreciable mammalian or phytoxicity value.

2-3 FORMULATION

Technical pesticides (90+ % active ingredient) generally are formulated prior to use except when they are liquids that can be sprayed neat (undiluted). Formulations include solutions, suspensions, powders, granules, or other forms designed to meet application needs and use requirements.

Van Valkenburg (1973) notes that several factors should be considered in formulation chemistry including (i) importance of the solubility parameters of the hydrophobic and hydrophilic portion of the surface-active agent in selecting an emulsifier, (ii) effect of the phase inversion temperature on emulsion stability, (iii) the dehydrating effect of fertilizer salts and emulsifiers and the resultant stability or unstability of the emulsion, (iv) the all important flowability property of a mixture as it relates to the development of a dry pesticidal formulation, (v) catalytic effect of clays and other carriers on pesticide degradation, and (vi) and the physical properties of formulations and how they affect the size of the particles in a spray and the movement of the particles in air.

The physical and chemical properties of the formulation and its resultant spray characteristics as indicated by particle size and surface properties (surface tension, spreading coefficient and contact angles) dictates whether the pesticide will adhere to the plant surface and penetrate

pesticide formulation types are wettable powder (WP), emulsifiable concentrate (EC), water miscible concentrate (WMC) and flowables (F). These are designed to be diluted with varying ratios of water and applied by various types of spraying equipment. Important properties of the active ingredient that affect its alternate formulation include physical states, water/oil solubility, miscibility, dissolution rate, melting point, density, and physical chemical stability to heat, oxygen, and moisture (Van Valkenburg, 1973). The pH both in the bulk and in solution/suspension of pesticide formulations is also important with mixtures of pesticidal ingredients or sometimes even with a single ingredient with additives to achieve desired physical properties, ease of application, and favorable metabolic efficacy. Formulation character affects stability of the active ingredient, ease of field mixing, bioavailability of active ingredient to the target organism, residuality of active ingredient and adducts, and potential side effects of pesticides. Certain aspects of pesticide formulation and use are subject to regulation by EPA and other government agencies.

Pesticide formulations are available in many forms permitting the use of a variety of equipment types -- ground vs. aerial application -- to control target organisms effectively and successfully. Pesticides are formulated rather than used directly because of the necessity (i) to dilute high-potency material to field concentration, and (ii) to apply them to a location where the target organism can be controlled while side-effect damage to humans, plants, wildlife, and the environment is minimized.

2-3.1 Emulsifiable Concentrates-Solution Systems

Most pesticides are dissolved in suitable oils or other organic

solvents, with emulsifiers added, and packaged as emulsifiable concentrates (EC). Typical EC formulations contain from 0.12 - 0.48 Kg active pesticide per liter (1-4 lbs gal^{-1}). Solution systems without emulsifier also are used, particularly for low-volume (LV), or ultra-low-volume (ULV) sprays. Emulsifiable concentrates are the bulwark product for pesticide sprays. They can be diluted with water and are simple to use. Low surface tension increases ease of atomization and impingement probability.

2-3.2 Wettable Powders, Granular Products, and Flowables

Wettable powders are produced by adsorption of technical pesticides on finely ground clay containing wetting agents. The resulting products are dispersible in water. Granular products containing a very high percentage of active ingredient have been formulated to alleviate some of the problems that occurred in handling wettable powders. Flowable products are finely ground, insoluble active ingredients suspended in oils with emulsifiers. They are non-dusting and can be pumped as viscous liquids.

Granular pesticides are pellets or grains containing the pesticide diluted to the permissible concentration by mixing with other inert and functional ingredients. Granular carriers are inert, sorptive particles with a size range of 4 to 200 mesh and are produced in two forms -- disintegratable (regular volatile material - RVM) and nondisintegratable (low volatile material - LVM) in water. The major advantages of granular formulation over dusts, wettable powders, water-soluble powders and liquids are that it (i) permits uniform application at desired rates, (ii) provides minimum dusting, (iii) delivers toxicant to desire location, (iv) either water disintegratable or nondisintegratable, (v) minimizes phytotoxicity, and (vi)

regulates pesticide release so to act as a reservoir to extend pesticidal activity for a longer period of time. Granular pesticides applied to the soil surface can be picked up and moved in overland flow offsite as a result of a high intensity rainfall event (Bailey et al., 1974).

Ground applicators for granular pesticides usually are attachments on row crop planters. They include capability for application in the seed furrow or a broadcast band over the row that either remains on the soil surface or is incorporated by some mechanical means. Effective operation requires that the applicator meters, delivers, and then distributes the pesticide granule over the soil or in some cases to incorporate them to the proper soil depths.

The granules generally are metered either through a gravity-fed metering orifice or through a positive metering device in which a constant granule volume is metered by a rotor. The granule is delivered to the target location by mean of gravity or pneumatic pressure.

2-4 PESTICIDE APPLICATION SYSTEMS

Most pesticides are applied by spray processes whose atomization (spray spectra) is dependent on nozzle type, pressure throughput, and other factors. Dusts are no longer widely used. High technology and engineered delivery systems need development, such as for controlled release (CR) of the active agent. In Australia, a new CR product emits a biodegradable, short-life insecticide within the root system of sugarcane (*Saccharum officinarum*) (McGuffog et al., 1984). It protects the first and successive rattoon crops up to 4 yrs. This delivery system meets a critical plant protection need, is highly efficient in pesticide delivery, minimizes ecosystem effects, and limits the build-up of resistance.

2-4.1 High Volume Dilute Spray Systems

High volume dilute sprays in the range of 400-3000 L ha^{-1} (100-800 gal $acre^{-1}$) are inefficient and labor and energy intensive. They operate by attempting to saturate foliage, often using turbulent, high velocity air streams. Large losses occur to the soil and to drift.

2-4.2 Low-Volume and Ultra Low-Volume Sprays

Spray volumes in the range of 4 to 40 L ha^{-1} (1-10 gal $acre^{-1}$) are often referred to as low volume (L). Ultra-low-volume (ULV) sprays produce < 2 L ha^{-1} (<0.5 gal $acre^{-1}$). These low volumes spray clouds reduce foliar runoff (foliage saturation). No low volume or ultra-low-volume spray, however, can provide "even coverage". Visual observations during spray application are widely believed to substanciate "even coverage" but have no actual validity. "Even coverage" is a visual illusion. Measurement of the actual coverage of typical foliage systems is complex and time consuming. It requires use of tracer sampling and analysis systems that meet suitable probability standards. In the case of foliage systems that have substantial vertical dimensions, i.e. forests and dense crops, deposition within the canopy falls to a few droplets per square centimeter. Transport and impingement in foliage from L and ULV sprays reflect turbulence within the canopy, the number of droplets in each size category, velocity of travel, geometry of the target, spray volume, foliage density and dimensions, and other factors. In typical cases, deposition is greatest on the tops of leaves or needles, on leaf hairs or insect setae, and on rough surfaces including leaf veins and insect appendages. Deposition on the underside of leaves is very low but increases

as turbulence increases. Insects and disease vectors that are resident on the underside of leaves represent a major pest management problem. In dense foliage, pest management often requires an increase in numbers of effective sized droplets. Specialized formulations may be required to maximize adherance and control on waxy surfaces.

The ULV sprays are increasing in use. The concept of ULV was developed to meet spatial and temporal problems in control of the desert locust during its migrational flights in inter-continental space measured in thousands of km^3 (Sayer, 1959). Numbers of droplets in a spray are an inverse cube function of size; hence, as spray volumes were reduced to meet logistic requirements, small size spray spectra were crucial. The original ULV concept involved a concomitant decrease in size of spray spectra and the volume of the spray; however, the significance of the size of the spray spectra was lost as ULV was adapted to agriculture using hydraulic nozzles.

As spray clouds diffuse, the numbers of droplets per cm^3 decreases, but lethal deposits can occur on insects when concentration of the pesticide in each droplet is high (Keathley, 1972; Himel, 1974). Volume-concentration factors in the design of insecticide spray programs are discussed by Spillman and Joyce (1978). Factors that control spray efficiency are discussed in sections 2-9 and 2-10.

Mosquito abatement groups have used ULV sprays for decades with typical applications of 60-120 mL of concentrated or neat insecticide per ha (1-2 oz $acre^{-1}$). Mosquito sprayers use special nozzles (centrifugal and pneumatic) that are designed to limit the production of droplets larger than 40-50 μm. Size specifications for pesticide sprays to meet public health needs are not in controversy. The size of aerosol droplets impinging on mosquitoes has been

reported by Lofgren et al. (1973) to center in the 5-10 μm range, conforming to impingement dynamics on a small, flying insect.

2-5 FOLIAR APPLICATION AND LOSS

Foliage or plant canopy may be the desired initial and final site for pesticide delivery. Plant canopy, as seen in Fig. 2-1 also may be the source of further pesticide transport to the soil or to the atmosphere. The latter may affect worker reentry and impose a human health risk. Characterization of this sink-source is necessary but has been lacking. Prediction of delivery and redistribution of pesticides within the plant canopy is the key to efficient use of pesticides. It requires a knowledge of pesticide spray physics, aerial transport phenomena, foliage intercept factors and storage; decay/transformation, plant uptake, and volatilization; and washoff behavior.

2-5.1 Initial Deposit of the Pesticide

Several factors influence the amount of initial deposit on the crop cover after application (Ripley and Edgington, 1983). The rate of application is the most obvious factor with increasing deposit occurring with increasing application rate. A limit is reached, however, beyond which no pesticide can adhere to the foliar surface. The amount of the deposit is slightly affected by the height of the spray boom above the canopy surface; a slightly lower amount of residue is found in the middle compared to the top of the plant canopy. The extent of ground cover is important, but plant surface characteristics, morphology, and surface area/plant mass ratio of the crop intercepting the pesticide spray also can result in a differential deposition over the crop. Formulation also affects residue deposit, and in most cases, a

lower amount of residue is found with wettable powders compared to emulsifiable concentrates or flowable formulations. Formulations may facilitate greater penetration, reduce early physico-chemical loss, and enhance foliar persistence. The amount of pesticide intercepted by the crop canopy is assumed to be proportional to the extent of ground cover at the time of pesticide application (Beyerlein and Donigian, 1979).

2-5.2 Pesticide Disappearance/Persistence

Persistence in this case is defined as the residence time of a pesticide in a defined compartment of the environment expressed in units of time relative to a bench mark (Greenhalgh, 1986). Pesticide persistence is the integrated effect or weighted summation of all the transformation and loss processes including chemical (e.g. hydrolysis), photochemical, and biological transformation; volatilization; cuticle adsorption; and washoff. Factors influencing persistence or the converse disappearance include crop factors (morphology, cuticle characteristics, stage of growth at treatment, and rate of growth) pesticide characteristics (Henry's law constant; water solubility; susceptibility to physical, chemical, and biological transformation processes) and environmental (rainfall intensity, duration and frequency; wind velocity; humidity; temperature; light-intensity; and percent cloud cover) conditions.

Disappearance curves after foliar application show an exponential decline for most pesticides. Pseudo first-order reaction kinetics may often be used to describe the decline in pesticide residue. One problem is that many such studies only treat a portion of the disappearance curve (time > 1 day) or only 1 to 2 half-life periods (generally five half-lives or more are preferred). Several mixed-order rate equations may be operating simultaneously because several different processes are involved and bi- or

trilinear curves have been reported (Ebeling, 1963). Many studies have failed to account for either the large initial residue loss (possibly because of volatilization, hydrolysis, or photolysis) in the early period after deposit (time < 1 day) or the apparent long persistence of low concentrations of pesticide in the plant. The application of regression analysis using semilog first-order approaches has not resulted in good correlation, particularly where two or more apparent first or even second-order processes are involved.

For the persistance of certain pesticides in plants Sirons et al. (1982) found a relation of C = k (a * b * log t) , where *k* = rate of disappearance, *t* = time after application and *a* and *b* are coefficients.

2-5.3 Washoff - A Specific Loss Pathway

Attempts have been made to study and, in certain case, to model the various dissipation or attenuation pathways. Washoff as an attenuation pathway will be discussed; little is known about the other pathways.

Several different approaches have been reported (Beyerlein and Donigian, 1979; Smith et al., 1981; and Willis et al., 1982) for describing the foliar washoff process for any rainfall event; the form generally is PWO = FP * WOC * R where : PWO = pesticide washoff (MT^{-1}), FP = foliage pesticide (ML^{-2}) i.e. kg ha^{-1}, WOC = washoff coefficient (L^{-1}), and R = rainfall (LT^{-1}). Several models have been proposed to account for or predict foliar washoff. Beyerlein and Donigian (1979) proposed an equation which describes the removal of pesticides from crops by rainfall as an exponential function of the rainfall intensity. Such an approach necessitates the use of hourly rainfall data and a crop constant based on crop and pesticide properties to determine the washoff coefficient. A foliar washoff algorithm is contained in the CREAMS model

(USDA, 1980) for predicting the proportion of pesticide lost from foliar surfaces. The residue is partitioned into dislodgeable (available for washoff) and non-dislodgeable fractions. Washoff is calculated for each rainfall incident from the dislodgeable fraction, less the amount attenuated, after a plant washoff threshold has been reached. The washoff threshold (0.1 - 0.3 cm) is the amount of rainfall that a plant canopy can intercept and store prior to washoff. Smith and Carsel (1984) proposed a pesticide washoff model (FWOP) which requires daily rainfall amounts (cm day^{-1}) and a lumped first-order rate constant for foliar transformation processes (k_f). Specific formulation includes:

$$\frac{d[FP(t)]}{dt} = - k_f FP(t) - PWO(t) + APP(t) \qquad [1]$$

where

$\frac{d[FP(t)]}{dt}$ = rate of change of pesticide on foliage

k_f = first-order degradation rate constant on the foliage (T^{-1})

$k_f = k_p + k_r + k_b + k_v + k_h$

k_p = rate constant for photolysis (T^{-1})

k_r = rate constant for chemical reactions

k_b = rate constant for biodegradation

k_v = volatilization rate constant

k_h = hydrolysis rate constant

and $PWO(t) = FP(t) * WOC * R(t)$ [2]

where

PWO(t) - pesticide washoff (MT^{-1})

FP(t) - foliage pesticide (L^{-1})

WOC - washoff coefficient (L^{-1})

R - rainfall (LF^{1})

and APP(t) - application rate (MT^{-1})

This equation cannot be solved analytically in a closed form because rainfall is stochastically variable in time. The equations therefore must be solved numerically as a part of a continuous simulation model. The FWOP model has been coupled with the Pesticide Runoff Simulation (PRS) (Computer Sciences Corporation, 1980) to make such calculations.

Willis et al. (1982) found that total storm losses from toxaphene on cotton (Gosspium hirstum) under simulated rainfall were independent of intensity when 24 mm of simulated rainfall was applied at the rate of 13, 25, 51, or 100 mm h^{-1} just 2 h after toxaphene had been applied at 2.24 kg h^{-1}. Approximately 5 to 10% of the toxaphene was washed off depending upon the initial load. Linscott and Hagin (1968) reported that mean losses of sprinkle-applied 2,4-DB were 21, 60 and 93 % of the amount on or in the plant when 2, 5, 13, and 51 mm of rain were applied, respectfully. A paucity of information exists on the loss of pesticides on foliar surface because of photolysis, volatilization, chemical, and biological transformation. Research is urgently needed to define those processes and pathways both to improve model formulation and to identify sources for pesticide availability in making risk assessment.

2-6 SOURCE TERM DESCRIPTOR FOR MODELING

A quantitative definition of the source terms is needed for modeling pesticide exposure and for making risk assessment. A general approach described by Bailey et al. (1974) will be updated and used to quantify the pesticide source term. The initial consideration in the description of the source term is the physical state of the pesticide and its spatial distribution with respect to the soil surface. Figure 2-1 shows that it may be (i) on the foliar surface, (ii) on the soil surface or (iii) incorporated into the soil and residing in the upper storage zone. The physical state of the pesticide is determined by the nature and properties of the formulation. Pesticide formulations as discussed earlier consist of five different physical types: solutions, wettable powders, emulsions, dusts and granular pellets. Their physical-chemical composition varies with the type and initial concentration of pesticide, solvent, surfactants/wetting agents, sticking agents, particle size distribution of the dust or wettable powder, and rate of release from the granular pellet. These factors influence pesticide-soil interactions and equilibria in the various storage zones and directly affect the availability of the pesticide for surface and vertical transport as well as its susceptibility to various transformation processes.

The source definition requires that the initial pesticide phase and spatial distribution condition as dictated by the application methodologies be categorized and quantified. Pesticides are directly applied to (i) the soil surface, (ii) incorporated into the soil, or (iii) purposefully or accidentally sprayed, dusted, or applied as granules/pellets to the canopy or to crop residues. Because of the restricted mobility of the pesticide, its initial placement is a crucial factor in mathematically describing the pesticide distribution on the foliage or pest surface, and on/or throughout

the soil profile, not only before and during the first rainfall event, but also between subsequent events. The initial placement also determines the relative importance of the four modes of transport - (i) mass transfer of the pesticide in the moving liquid boundary ; (ii) pesticide desorption into or towards the moving liquid boundary; (iii) stationary dissolution and transfer to the moving liquid boundary; and (iv) moving dissolution in the moving liquid boundary -- into runoff water. Initial placement determines whether the source is planar (initially surface-applied or subsequent foliar washoff onto the soil surface) or volumetric in nature (incorporated). Depth of incorporation and homogeneity of mixing (influenced by type of incorporation tool used) also influence the effective source concentration.

In the case of either directed or accidental foliar application the soil source term description is further complicated because of such processes as foliar interception, direct foliar drip, delayed foliar washoff and the various transformation processes - photolysis, chemical (e.g. hydrolysis) and biological -- volatilization, and plant or pest uptake and metabolism prior to reaching the soil surface. The role of atmospheric source characterization as a transport media is reviewed by Medved (1975). Pesticides released in the environment via spraying -- either aerially or via ground sprayers - pass to the target plant, pest, or soil, but some are carried away by the wind both horizontally and vertically for varying distances. These offsite sprays may either settle upon the soil surface or be deposited in rainfall (Fig. 2-2 -- secondary transport processes).

Gohlich (1983) defines the key features of the pesticide application distribution systems which need to be considered in reducing the amount of drift to include spray atomization and transport distance between atomizer and

receptor area. Atomization is influenced by physical properties of the liquid, types of nozzle, and the atomization process. Transport is influenced by air turbulence, size of particle, evaporation behavior of the liquid particle, direction and force of the flow stream and particle motion, and forward speed of the spraying device. Drift and deposit are influenced by structure of the plant or receptor and its density and by turbulence within the canopy. The latter is related to external wind velocity.

2-7 PESTICIDE SOURCE CHARACTERIZATION AND RISK ASSESSMENT

Risk assessment is a tool used to evaluate the probability of an adverse impact that a pesticide, being a toxic or hazardous chemical, may have on human health or the environment. The key role that a knowledge of the physical state of the pesticide and its spatial distribution with respect to the soil surface can be seen in Fig. 2-1. The role of management practices on pesticide transport and transformation can be seen in Fig. 2-2 and 2-3. These interactions determine which environmental pathways are crucial to the estimation of both human and biological exposure and the calculations of environmental risk. This topic is discussed at greater length in Chapter 13.

2-8 PRINCIPLES OF PESTICIDE SPRAY PHYSICS

The developing science of pesticide spray physics is concerned with the complex interactions of spray droplets in a spray cloud and during impingement. These interactions occur (i) during transport in the air (includes both turbulent transport and sedimentation ; (ii) at the foliage-air interface (includes impingement probability and impingement filtration; and (iii) within the canopy (includes impingement probability, target geometry,

turbulence within the canopy, and impingement delivery).

Droplet impingement involves (i) size of the droplet, (ii) velocity of travel, and (iii) geometry of the substrate. A droplet large enough to have a critical impingement velocity of zero (impingement probability = 1) will impinge on a target of any geometry at zero velocity. Penetration into a foliage canopy requires an impingement probability < 1.

The hydraulic nozzle is used in most aerial and ground spray equipment because it is cheap, widely available, and because there has been no substantial pressure for change to more efficient delivery systems. Hydraulic nozzles atomize spray liquids into thin sheets and filaments and subsequently into a random, polydisperse spectrum of droplets whose sizes range from submicron to large. The distribution frequency approximates a bell-shaped, gaussian curve. A significant portion of the pesticide controversy stems from the fact that these large-droplet, broad spectrum sprays are grossly inefficient in transport of pesticides to target foliage. Its inefficiency and environmental costs are not widely recognized. Spray physics evaluates the transport and impingement characteristics of each size class of droplets in a polydisperse spray cloud. For all practical purposes, spray spectra can be divided into two size classes:

(i) Small droplets (< 100 - 150 μm diameter).

(ii) Large droplets (> 150 μm diameter, ranging to 400 - 600 + μm).

The significance of these two size classes is that small droplets as a class are transported primarily on turbulent eddies and have an impingement probability < 1. Their impingement on target systems depends on droplet size, travel velocity and the geometry of the target. On the other hand, the

primary force acting on large droplets is gravity. They have an impingement probability P = 1 and impinge on the first solid or liquid substrate in their flight path. Typically, this means that they are delivered to peripheral foliage or the ground.

The objective of most pesticide spray applications is to deliver the spray cloud to a foliage target. Herbicide sprays are directed at any portion of the target plant whereas most insecticide and fungicide sprays are directed at microhabitats within the foliage canopy. Spray clouds are difficult to measure and portions of the spray are invisible. An empirical spray technology based on the use of polydisperse sprays was developed in the early and middle decades of the 20th century. It was "successful" and appeared to be "simple". It was buttressed by the visual illusion that spray clouds "fell" into the foliage. The actual interaction of spray clouds with the foliage canopy and the mechanism of pest control from sprays was unknown. This conventional spray technology was developed in an analytical void since nanogram sensitivity gas chromatography (GC) was not developed until 1959 and analytical methods for spray mass transport were not developed until the late 1960s. Spray physics became a part of pesticide controversies only in the decades since 1970.

In this part of Chapter 2 we will discuss at length the role of mass transfer as the initial step by which pesticides are introduced into the environment. This is a different approach from those which relate to the study of pesticides <u>after</u> their original transfer. Controversies focus on the significance of droplet spectra in spray clouds, the mechanism of delivery of sprays, effects of a foliage environment, pesticide volatility, redistribution, and spray drift.

Spray physics provides one simple, overriding guide to pesticide use -- efficient delivery of pest management sprays is size-limited. This is because foliage systems present a narrow, size-limited "window of opportunity" for pesticide sprays. The upper size limit is determined by impingement on peripheral foliage and the lower size limit by impingement probability within the canopy. All broad spectrum sprays overlap that window and are therefore "successful", whatever may be their economic and ecological limitations.

2-8.1 Spray Propagation.

Mass transport and impingement can now be measured for all discrete spray droplet spectra which travel as a spray cloud. This includes spray clouds which are electrostatically charged but excludes chemigation and high volume sprays which saturate and "run-off" from foliage. As spray clouds move away from their source, they expand as droplets within the cloud and are subjected to turbulence and gravitational forces. Turbulence is a key factor in the transport of "small" spray droplets. Large droplets and light refraction allow spray clouds to be seen. Under typical spray conditions turbulence and sedimentation causes the spray cloud to move in an expanding, usually downward pattern.

Although it is well known that the ground under a tree remains dry after a "light rain", the "light rain" of a pesticide spray at the foliage-air interface is assumed to "penetrate" and to provide "even coverage" within the foliage canopy. Although nature had provided a clue in the size-related transport and impingement of air-borne pollen and although the engineering physics of air filtration of particulates was well known, no interdisciplinary transfer of physical principles occurred and spray physics played no part in

an empirical, simplified, conventional spray technology which was accepted worldwide without any analytical basis.

To some significant extend this is because of spray drift. Spray drift is a fact. However it typically constitutes < 5% of the mass of most sprays and is dwarfed in potential ecological significance by losses (60-80%) of most pesticide sprays on peripheral foliage or to the ground (Table 2-6). The direct effects of spray drift can be seen. The ecological and economic significance of pesticides wasted and transferred to the soil, is difficult to measure or assess.

The typical assumption of spray drift is that it stems from downwind transport of "small" droplets in the spray cloud outside the spray area. Volatility, evaporation, and secondary transfer effects are not considered. The ubiquitous presence of "small droplets" in the foliage canopy was unknown or ignored. Analytical proof of the delivery of "small" droplets into foliage canopies is the crux of the analytical data provided in the case studies in this chapter. These case studies require some knowledge of spray spectra. Spray spectra measurements include:

D_{max} - the diameter of the largest droplet in the cloud, as estimated.

MMD (VMD) - the mass median diameter (volume median diameter). The diameter that separates the spray (mass or volume) into equal parts.

NAD - number average diameter, the average size of all spray droplets measured.

Most pesticide sprays have a D_{max} of 300 - 600 μm with a concomitant MMD in the range of 125 - 400 μm. Broad spectrum herbicide sprays have a D_{max} of

1000 μm or more. Grover et.al. (1972) and Barry (1984) have reported on the distribution of sizes in sprays.

Pesticide spray transport and impingement is controversial. Two theories (sedimentation theory and turbulence theory) have been used to explain the effects of pesticide sprays. The multibillion pound pesticide spray industry is largely guided by sedimentation theory. Turbulence theory was developed after 1970. It represents a basis for optimization of pest management and risk management of drift. The two theories diverge in their predictions as to the bioefficacy of large-size and small-size portions of spray clouds. In this divergence, the theories are mutually exclusive; both cannot be correct. The case studies cited in this chapter provide an analytical basis for turbulence theory. A brief review of sedimentation and turbulence theories is given below.

2-8.1.1 Sedimentation Theory

Sedimentation theory is empirical and has no rigorous analytical basis. It evolved prior to development of analytical systems for mass transport of sprays. Its primary concept is Stokes Law of Falling Spherical Bodies and a Reynolds number < 0.1. It assumes that gravitational forces are predominant even in a cross wind. Some of its concepts are depicted in Figure 2-5. "Small droplets", having minimal mass are assumed to travel "an infinite distance." If "small" droplets "blow away", large droplets must then provide the pest management which is observed. Actually impingement probability limits spray droplet access in and on foliage systems and thus the validity of sedimentation theory.

The theory gained credibility because of the visual illusion of spray clouds "falling" into foliage systems. The drift problem reached a critical stage in the use of herbicide sprays and was solved by the use of "ultra large" spray spectra with a D_{max} as much as 1000 μm without recognition of transport inefficiency and ecological effects. As an empirical theory, it has no analytical base and is an anachronism in a scientific century.

2-8.1.2 Turbulence Theory

Turbulence theory stems from principles of spray physics and the mass transfer analytical data presented in the case studies in this chapter. The theory assumes that mass transport of spray droplets in a spray cloud is the vector resultant of turbulence and gravitational forces. As droplet size decreases, the contribution of turbulent forces increases. Transport and delivery patterns of spray droplets in spray clouds are determined by turbulent diffusion and sedimentation. Spray droplets move in envelopes of sizes determined by the extent of turbulent forces (Fig. 2-4). Spray efficiency and spray drift are inversely related dependent variables. Spray efficiency is a determinant in risk management of drift.

The key to efficient pest management lies in favorable turbulence and optimization of the size of the spray spectra used. Data for optimum spray droplet sizes are found in the case studies cited in this chapter. Computer-aided spray models such as those discussed in Section 2-11 involve turbulent forces. Turbulence can be either favorable (average downward) or unfavorable (average upward). Favorable turbulence can maximize pest management and minimize drift.

Where the Reynolds number is > 0.1, the terminal sedimentation velocities in Table 2-7 depict rates of gravitational fall only for large droplets. Sedimentation and turbulence calculations for spray cloud transport are shown in Fig. 2-4. The wide divergence in transport calculated by sedimentation and turbulence is illustrated. Under the conditions cited sedimentation predicts that a 40 μm droplet will travel 5,000 meters downwind while turbulence indicates a downwind travel in a Gaussian envelope centering at 300 meters, not significantly different from the downwind travel of Gaussian envelopes containing droplets from 10 - 300 μm in diameter.

2-8.2 Estimation of Droplet Size Distribution

Numerous investigations have attempted to relate liquid characteristics, nozzle type and size, and boom pressure to the prediction of spray droplet size distribution during the atomization process. Spray ejected into still air or air in streamline flow is not identical to that developed in turbulent air stream, which has additional shear effects (Miller 1980).

The following model can be used to estimate the size and number distribution of the spray from measures of the VMD (volume median diameter) and to estimate the spray cloud size-number distribution from spray recovery data. The computations follow the description of Saucier (1981) and Miller (1980) and are based on the hypothesis that the initial number of subclouds (sc), each of which contain a small range of droplet sizes. By making use of the droplet size distribution, the range of droplet sizes contained in each sub-cloud is replaced by a single representative size, defined by the median size of the droplet in the column. The number of droplets and the volume of spray contained in the sub-cloud is held fixed during this process. The mean

volume droplet size is specified by the average diameter (D_{sc})(μm) and is given by:

$$\bar{D}_{sc} = 2 \left[\frac{4}{3} \pi \int_{D_1}^{D_2} N \left[(D)\ dD \right]^{-1} \int_{D_1}^{D_2} dV \right]^{1/3} \qquad [3]$$

where D_1 and D_2 denote the lower and upper bounds, respectively, of the droplet sizes contained in the original subcloud.

If V_f represents the total volume of spray (mL) per unit distance (cm) along the flight line in droplet form and N represents the total number of droplets, then N(D), the number distribution as a function of droplet diameter is given by:

$$N(D) = V_f(D) \left[\frac{4}{3} \pi \int_0^{\infty} \left[\frac{D}{2} \right]^3 f(D)\ dD \right]^{-1} \qquad [4]$$

where f(D) denotes the droplet size distribution of the spray cloud.

Figure 2-6, adapted from Akesson and Yates (1974), shows observed droplet size distributions for a variety of spray types and nozzles with a logarithmic vertical drop-size scale. The near linearity of the plots illustrates the validity of log-normal distribution for modeling the size distribution. Using the log-normal assumptions, the droplet size distribution is given by:

$$f(D) = \frac{1}{\sqrt{2\pi}\ \sigma_n\ D} \exp \left[-\frac{1}{2} \left[\frac{\ln D - a}{\sigma_n} \right]^2 \right] \qquad [5]$$

where

$a = \ln(VMD)$ (volume median Diameter)

$\sigma_n = \ln(\sigma_o)$

σ = standard deviation

Substituting and integrating yields the number of droplets (nsc) and the volume (Vsc) which lie in the subcloud (sc) range D_1 to D_2:

$$n_{sc} = \frac{3V}{\pi} \exp\left[- 3a - \frac{9\sigma_n^2}{2} \right] \left[\operatorname{erf}\left[\frac{\ln(D_2) - a}{\sigma_n \sqrt{2}} \right] - \operatorname{erf}\left[\frac{\ln(D_1) - a}{\sigma_n \sqrt{2}} \right] \right] \quad [6]$$

$$V_{sc} = \frac{V}{2} \left[\operatorname{erf}\left[\frac{\ln(D_2) - (a + 3\sigma_n^2)}{\sigma_n \sqrt{2}} \right] - \operatorname{erf}\left[\frac{\ln(D_1) - (a + 3\sigma_n^2)}{\sigma_n \sqrt{2}} \right] \right] \quad [7]$$

The mean volume droplet diameter of any sub-cloud can be computed from the following:

$$D_{sc} = 2 \left[\frac{4\pi V_{sc}}{3n_{sc}} \right]^{1/3} \quad [8]$$

2-8.2.1 Effects of Evaporation on Droplet Size

The evaporation of water-based droplets plays an important role in determining the size of spray droplets on impaction, or the final size of

droplets in the droplet spectrum. Because of the substantial difference in rates of evaporation as a function of size, highly diluted sprays end with a skewed spray spectrum that increases spray drift.

An effective droplet size distribution can be computed based on the time to maximum deposition computed from the model and the thermodynamic relationships based on the relative humidity and droplet viscosity. The effective droplet distribution is directly related to the droplet distribution resulting from each specific nozzle configuration by partitioning the droplet into a number of discrete levels. A correction factor is applied separately to each level to derive an effective characteristic diameter for each level.

The effective droplet-size distribution by number is related to the droplet size distribution at the exit of the nozzle. Droplet size changes because of mass transport during the delivery. A serious drawback of dilute, water-based sprays is the potential for droplet size reduction by evaporation and the potential for skewing the droplet spectrum toward sizes that are not filtered out by foliage (< ~5 μm). The time rate of change of a water droplet diameter is given by the following relationship adapted from the work of Trayford and Welsh (1977):

$$d = d_o \left[1 - \frac{t}{t_1} \right]^{1/2} \qquad [9]$$

where

d = droplet diameter (μm) at time t after release

d_o = initial droplet diameter (μm)

t = time after droplet release (sec.)

t_1 = expected lifetime of droplet (sec.)

The expected lifetime of the droplet is given by:

$$t_l = \frac{d_o^2}{\lambda w_d} \qquad [10]$$

where

w_d = Wet bulb depression (° C)

For water droplets,

$$\lambda = 84.76 \left[1 + 0.24\ R_e \right]^{1/2} - 10^{-12} \qquad [11]$$

where

R_e = Reynolds number of the non-evaporated droplet

The expected lifetime of the droplet (K_d) is given by the following equation derived by Amaden (1962):

$$t_l \approx \frac{d_o^2}{80\ \Delta T} \qquad [12]$$

where

ΔT = the difference in temperature (°C) between wet and dry bulb thermometers commonly called the wet bulb depression.

For example, at a wet bulb depression of 17°C, a 600 μm droplet has an expected lifetime of 264 sec.

2-8.2.2 Extrapolation to Non Aqueous Formulations

Evaporation of spray formulations which contain no water can be calculated considering the basic thermodynamics in the evaporation processes. The rate of evaporation is inversely related to the amount of heat which must be transferred from the surrounding air to evaporate a unit volume of spray. Therefore, differences in the amount of heat required to vaporize a unit volume of non-water spray material vis-a-vis that for water must be accounted for in computing the expected lifetime of the spray droplet based on water spray data and equations. In addition, the rate of evaporation is directly proportional to the difference between the saturation vapor pressure of the spray material, evaluated at the air temperature and the partial pressure of spray vapor already in the atmosphere.

For volatile sprays other than water, the following relationship gives the expected lifetime of a droplet:

$$\gamma_l = \left[\frac{L}{L_w}\right]\left[\frac{P_{sw} - P_{air}}{P_s}\right] \gamma_{lw} \qquad [13]$$

where

L = Latent heat of evaporation of spray (J)

L_w = Latent heat of evaporation for water (J)

P_{sw} = Saturation vapor pressure of water at evaluated air temperature (P_a)

P_{air} = Partial pressure of water vapor in the air

P_s = Saturation vapor pressure of spray evaluated at air temperature (P_a)

γ_w = Expected lifetime of a water droplet (sec)

2-8.3 Stokes' Law and Spray Cloud Sedimentation

Sedimentation velocities of pesticide spray droplets are usually calculated from Stokes' law (Table 2-7). Sedimentation calculations shown in Table 2-7 have no actual validity where droplets are small (<100 μm). They are usually transported on turbulent eddies, rather than by sedimentation when Reynolds numbers are < 0.1, i.e., under most field spray conditions.

The Reynolds number and the terminal velocity of a droplet in free flight are related functions. The Reynolds number for any particular droplet size is computed from knowledge of the terminal velocity of the spray droplet as:

$$R_e = \frac{e_a \, V \, D}{h} \qquad [14]$$

where

R_e = Reynolds Number

e_a = density of the air (mg m^{-3})

V = terminal or settling velocity (m sec^{-1})

D = droplet diameter (μm)

h = kinematic viscosity of the air (N sec m^{-2})

A droplet in free fall will accelerate downward until the gravitational force exerted on the droplet is counterbalanced by aerodynamic drag forces caused by the movement of the droplet through the viscous atmosphere. When these forces are in balance, the droplet then falls at a constant rate called the terminal or settling velocity of the droplet.

The terminal velocity is controlled by the coefficient of drag of the particles which, in general is a nonlinear function of the Reynolds number. For the particle sizes common to aerial sprays, however, it is only appropriate to operate in the lower regime of Reynolds numbers in which the coefficient of drag of spherical particles is well represented by a linear approximation. In this regime the settling velocity can be determined from Stokes' law. The settling velocity (V) given by Stokes' law is:

$$V = \frac{g\ D^2\ e_d}{18\ h} \qquad [15]$$

where

V = settling velocity (m sec^{-1})

g = gravitational acceleration = 9.8 m sec^{-2}

D = droplet diameter (μm)

e_d = specific gravity of the spray liquid (kg m^{-3})

h = absolute viscosity of the air (181 N sec m^{-2})

The major factor determining the terminal or settling velocity of a droplet and thus its potential for turbulent transport is the droplet size. Table 2-7 presents the calculated terminal velocity for different size droplets (assuming laminar conditions and low Reynolds numbers).

In the case of liquids, the larger droplets may be deformed by aerodynamic forces that can reduce their terminal velocities below that shown.

2-8.3.1 Turbulent Transport

Turbulent forces are significant in transport of spray clouds whose

droplets are < 100 μm (Glotfelty and Caro, 1975). Under favorable meteorological conditions, i.e., no thermal upwelling, turbulent transport carries the spray cloud downward into the foliage canopy. The greater the turbulence, the faster the transport and the greater the probability of reaching the foliage canopy and being filtered out within that canopy. This is a factor that underlies minimization of drift as cross wind speed increases.

The effect of turbulent transport on the drift and deposition of the spray cloud can be visualized by considering a sedimenting cloud as diffusing around its center of gravity and can be related to a line source spray cloud release in the lower 15 m of the atmosphere. Initially, the spray cloud follows a linear growth pattern primarily based on dispersion. Comparisons of the results of experiments using tracer distribution and independent comparison with spray data show good agreement with the assumed linear growth law and intensity of meteorologically derived atmospheric turbulence.

Models based on classical diffusion equations tend to underestimate the speed of growth of real spray clouds. Attempts to correct this effect by superimposing a pseudo-sedimentation velocity have been attempted but have not proven to be satisfactory. Bache and Sayer (1975) provided an empirically derived scaling factor to compensate for this effect. Empirical data, by Bache (1975), indicate that an appropriate scaling term for spray deposition was related to the location of the position of the spray cloud concentration maximum near the surface. This relationship is illustrated in Equation [16]:

$$\left[\frac{\sigma}{\sigma_m}\right] - g\left[\frac{x}{x_m}\right] \qquad [16]$$

where

σ = the standard deviation of the cloud distribution

x = downwind distance (m)

m = subscript for maximum

g = acceleration because of gravity (9.8 m sec^{-2})

This result is supported by the work of Csanady (1973) and Jobson and Sayer (1970) related to the description of a diffusing cloud with sedimentary type settling. For droplets with relatively slow settling velocities, the concentration as a function of height and time is described by Equation [17], which is related to standard Gaussian dispersion considerations for an elevated line source.

$$C = \frac{Q}{\sqrt{2\pi}} * \frac{2hz}{\sigma^3} * \exp\left[- \frac{h^2}{2\sigma^2} \right] \qquad [17]$$

where

C = concentration (droplets ml^{-1})

Q = source strength (droplet ml^{-1})

h = height of release (m)

z = height (m)

σ^2 = variance about center of cloud

σ = standard deviation

Differentiating Equation [17] and equating the result to zero yields the following conditions for maximum concentration, $\sigma = h/\sqrt{3}$. Therefore, the maximum concentration is:

$$C_m = Q \sqrt{(2/\pi)} * \frac{z}{h^2} \left[\frac{3}{e} \right]^{1.5} \qquad [18]$$

A knowledge of the cloud growth is a key factor in the description of airborne concentration at or near the ground level. Generalizing the exact relationship between cloud growth and airborne concentration is described by the linear relationship, cg = b i x. [19]

where

cg = cloud growth (m)

b = a constant of proportionality which is empirically derived

i = the turbulent intensity

x = downwind distance (m)

Therefore, the coefficient b can be written as a function of x_m (the downwind distance of maximum concentration), *h* and the turbulent intensity *i* and is given by Equation [20].

$$b = \frac{h}{\sqrt{2}\, x_m\, i} \qquad [20]$$

Bean (1971) has developed an expression for turbulent intensity *i*, which is related to wind speed, *w*, for neutral to unstable atmospheric conditions, and where u is equal to wind speed at normalized height.

$$i = \frac{\sqrt{w^2}}{u} \qquad [21]$$

2-8.4 Pesticide Spray Impingement

All spray droplets have finite impingement probabilities ranging from ~0 to 1 (from ~0% to 100%). The velocity required for impingement is termed the critical impingement velocity. Large spray droplets have a critical impingement velocity ~0 and an impingement probability = 1 (100%). They impinge on peripheral foliage or fall to the ground. As droplet size decreases from the range of 100-150 μm, probability of impingement decreases i.e. becomes < 1. As the probability of impingement decreases, critical impingement velocity increases and the actual point of impingement becomes a function of the droplet size, capture cross section, velocity and turbulence and depends upon the size, geometry, and biology of the target. A significant number and mass of droplets < 100 μm penetrate through the foliage barrier and enter insect and disease vector microhabitats.

Filtration is related to foliage density. Needles in conifer foliage are efficient filters. Filtration by broad-leaf foliage has not been quantified but appears to be related to density, shape, leaf hairs, veins, roughness, cuticle wax, and edge effects.

2-8.4.1 Spray Drift and Spray Efficiency/Efficacy

Spray drift is a complex scientific, social, economic, environmental, and legal problem. It involves principles of both spray physics and risk management. Based on a survey, the National Aeronautics and Space Agency reported at a NASA 1980 spray conference that aerial spray operators considered spray drift to be their most important problem. Early concepts of spray drift were reviewed by Akesson and Yates (1964). For our purposes,

spray drift is defined as those air-borne components which move downwind and outside of the defined spray area. Since almost all pesticides are volatile, primary drift consists of particulate pesticide and pesticide vapor. It can be divided into near-field (short range) and far-field (long range) drift.

Secondary drift occurs post-spray and consists of vaporization from soil and foliage plus the aerial movement of soil-pesticide particulates (Fig. 2-7). All sprays, no matter how broad their spectrum, contain a driftable component. When aqueous sprays are highly dilute, evaporation occurs rapidly with droplets smaller than 150 μm (Spillman, 1984). This skews the resultant droplet spectrum, producing a wide range of small particulates that exacerbate drift problems.

The small droplet portion of the spray cloud is delivered by turbulent eddies. Its insecticide-fungicide bioefficacy depends on ability to circumvent impingement at the foliage barrier and a concomitant ability to deliver active agent to biological targets within the foliage system. Efficacy is limited to the portion of the spray mass that reaches biological targets. Drift constitutes vapor plus those droplets that do not fall to the ground or are not filtered out by foliage. Efficacy and drift are thus inversely related dependent variables. As spray efficacy is increased, the total amount of pesticide required is decreased with a concomitant decrease in spray drift and ecosystem burden. Spray drift is a probability problem, subject to risk management principles.

In the past it was assumed that since small droplets have long calculated sedimentation times they "drift" far downwind. This is aptly illustrated in Fig. 2-5 (Akesson and Yates, 1984). Based on sedimentation calculations, droplets < 100 μm in diameter are labeled "drift-loss-indefinite

distance." The spray concepts shown in Fig. 2-5 have no analytical basis but cast a wide shadow over the pesticide use industry, acting to eliminate scientific progress in this worldwide industry.

Sedimentation is a widely used assumption in the spray efficacy literature. That literature is immense and largely without a quantitative basis. Spray spectra are usually unknown or unreported. Typically, bioassays of mortality are made, post-spray, without any knowledge of the actual sizes of droplets in the broad spectrum spray or what produced the mortality that was measured. Much of this literature which ignores underlying principles of spray physics is obsolete and a barrier to scientific progress.

The biological efficacy of pesticide sprays is determined by the efficiency of primary delivery and secondary redistribution. All spray droplets contain pesticide and, if delivered, can contribute to accumulation of a lethal dose by the target. Pesticide spray management is a really a problem in delivery probability in the use of polydisperse pesticide sprays in turbulent air streams.

The crux of pest management lies in recognition of the "window of opportunity" which is determined by probability of impingement and efficiency of delivery. Eckblad and Barry (1983) use this concept in optimization of forest sprays. When turbulence is low, droplets less than of 5 μm have a limited probability of impingement, i.e., they flow around the target. Velocity required for impingement defines the lower droplet size limit within the window of opportunity. The upper droplet size limit is determined by the efficiency of delivery. Efficiency of delivery into foliage microhabitats is size-limited to droplets < 100-150 μm. This is the upper range of efficiency for non-systemic insecticides and fungicides.

Herbicides are bioactive on any foliage, thus herbicide sprays are generally not size-limited. However, their efficiency is size-limited because mass delivery to peripheral foliage appears to peak in the range of 250 μm. As the size of droplets of herbicide sprays is increased, their efficiency falls. Droplet size and mass transport relationships in herbicide sprays have never been quantified. Droplets > 150 μm in diameter have a probability of impingement = 1 (100%), impinging on anything in their flight path. They are filtered out at the foliage-air interface or fall to the ground. Large droplets, contain most of the total mass in the spray, have a low delivery probability and a low bioefficacy. Most fall directly to the ground. Actual analytical data on droplet transport and impingement are reported in tables 2-2 to 2-5 and in Fig. 2-6.

The conifer forest can filter out spray droplets larger than ~5 μm (Crabbe et al., 1980a). They measured drift under these conditions to total < 5 % of a spray having a D_{max} of 58 μm and showed that spray loss to drift (spray droplets < 5 μm) along with volatilized pesticide can constitute the major portion of long range drift (far field drift). Increase in turbulence enhances delivery to forest foliage and decreases losses to the ground (Joyce and Spillman, 1978). As turbulence increases, delivery efficiency and foliage impaction increases and less pesticide is lost to the ground.

The efficiency of spray application is defined in Equation [22].

$$\text{Efficiency} = \frac{\text{Effective Mass Delivery}}{\text{Total Mass Spray}} \qquad [22]$$

Factors involved in spray losses are outlined in Table 2-6.

Efficient mass delivery in pesticide sprays is that which is delivered to targets. Present spray technology centers in the use of hydraulic nozzles

in which up to 75% or more of the spray has a low bioefficacy. Replacement of the hydraulic nozzle is a significant barrier to change because no alternative hardware has been widely accepted and no overriding pressures are acting to focus change.

Drift is also an impediment to change, e.g., the use of "still" conditions during spray application has been a "safe refuge" in the "fight against drift". Analytical data which show an increase in drift under still conditions have a basis in spray physics but no standing in current pesticide regulation.

Three factors which affect pesticide losses during spray application are estimated in Table 2-6. Reduction in delivery losses constitute the major potential for effective change in pest management.

2-9 PROPERTIES OF THE CANOPY ENVIRONMENT ON SPRAY INTERACTION

The properties of the canopy and the microenvironment surrounding the canopy have a large influence on pesticide deposition and behavior.

2-9.1 Physical Properties of Canopy

The deposition of spray within the canopy is dependent upon the structure including, leaf (needle) area and geometry, orientation, veins, edges, hairs, and stem diameter. Plant and/or tree spacing, and canopy density are also significant factors. Needles, edges, veins,and hairs maximize impingement. The smaller the droplet size, the lower the collection efficiency for any given target. The smaller the target, the greater its spray efficiency (Equation 22). The greater the crop density and roughness,

the larger the bulk removal of spray. The greater the turbulence, the greater is the foliage deposition. Far field drift is often composed of particulates < ~5 μm plus pesticide vapor. Still air increases drift (Crabbe et al., 1980a). Spray drift can be minimized as wind velocity increases (Joyce et al., 1979).

The turbulence regime within the canopy is different from that which occurs above the canopy. The collection efficiency of foliage or a crop canopy requires consideration of the probability that a droplet will hit an object (leaf or stem). Droplet collection efficiency within the canopy is directly related to the free stream air velocity, and the droplet size and inversely related to a representative foliar dimension :

$$E \propto \frac{e\ V_o\ d^2}{18\ h\ l} \qquad [23]$$

where

E = collection efficiency

e = droplet density (g cm^{-3})

V_o = free stream air velocity (cm sec^{-1})

d = droplet diameter (μm)

h = air viscosity (N sec m^{-2})

l = representative foliar dimension

2-9.2 Micrometeorological Factors

For spray droplet sizes where gravitational sedimentation is the predominant mechanism, the vertically falling droplets could fall on horizontal surfaces of the canopy, pass directly through the canopy, or bypass

the canopy and fall to the ground. The smaller the droplet the greater is the effect of horizontal components of airflow. Therefore, a droplet falling with a sedimentation velocity (V_s) affected by a horizontal wind (V_h) will approach a horizontal surface at the angle $\alpha = \tan^{-1}(V_s/V_h)$. This indicates that the effect of sedimentation is greatest for low wind speeds.

Since the wind is generally horizontal, droplets are more disposed to impact vertical surfaces. Further, because the smaller droplets are more strongly influenced by the wind, they generally have a greater potential for inertial impact. Bache (1975) indicates that for very small droplets (< 10 μm) inertial impaction is the dominant factor over almost all windspeeds.

The wind velocity is rapidly attenuated within the crop canopy. At the top of the canopy, if the wind velocity is strong, the predominant deposition mechanism is by inertial impact on vertical surfaces. Down in the canopy where the wind velocity is low; the predominant deposition mechanism is sedimentation on horizontal surfaces or by turbulent transport. Figure 2-6 illustrates the influence of a forest canopy upon the windspeed profile.

The average velocity required for prediction of spray drift and delivery is a function of the local canopy and can be estimated by extension from near ground meteorologic measurements. Extension requires knowledge of the wind profile as a function of height. The wind profile within a plant canopy can be approximated by the application of exponential scaling with height:

$$u = A \exp\left[\gamma(R - z) \right] \qquad [24]$$

where

u = windspeed at normalized height (m sec^{-1})

A = windspeed at the top of the canopy (m sec^{-1})

R = normalized height (m)

z = height above the ground (m)

γ = extinction coefficient whose value increases with canopy density. (ranges from about 1 to 5 for most naturally occurring vegetation canopies)

Above the canopy, the wind profile has logarithmic scaling and is approximated by:

$$u = \frac{u^*}{k} \ln(10R) \qquad [25]$$

where

u = windspeed at normalized height R > 1

u^* = wind friction velocity (m sec^{-1})

k = von Karman constant = 0.4

R = normalized height (m)

z = height above ground (m)

The average velocity in the profile between the ground and the application height can be found by integrating the scaling equations with respect to R, the normalized height, over the applicable limits and dividing by the normalized application height, R_{app}, as follows:

$$\bar{u} = \frac{\lambda}{\gamma R_{app}} (1 - \exp(-r)) + 0.435A \left[1.303 \left[1 - \frac{1}{R_{app}} \right] + \ln(R_{app}) \right] \qquad [26]$$

The potential biological effect of each spray droplet in the spray cloud

is dependent on both its transport pathways and its point of impingement. Impingement probability determines whether the spray droplet can penetrate the foliage barrier. Impingement probability also is a significant element in mathematical models being developed for computer modeling of pesticide sprays. Both validated mathematical models and the design of computer-aided spray processes will act as a guide for the recommended use of pesticide delivery systems.

The transport and impingement properties of pesticide spray droplets are predictable as a function of their size. Pesticide efficiency depends on both probability of transport to the target and probability of impingement on that target. Collection efficiency is represented in Equation [22].

2-9.3 Spray Delivery to Canopy

Environmental and economic considerations make it important to manage the aerial application of pesticides for maximal pest control and minimum use of resources. Zones of potential damage from pests are both contiguous to and commingled with non-target but sensitive areas. One method currently used for protecting sensitive areas is the establishment of *buffer zones*.

Pesticide spray released from aircraft or ground sprayers may, under various meteorologic conditions, drift into areas of sensitive vegetative and animal species. Pesticide applications must be carried out in an optimal manner so that minimum quantities of active ingredients will produce the maximum beneficial results. Two parameter requirements needed during both planning and operations are: (i) data that determine the pesticide drift characteristics; and (ii) data that define and/or characterize the risks attendant upon pesticide encroachment upon non-target areas.

Factors important to establishing drift characteristics include the following : (i) wind speed and direction ; (ii) droplet density and size distribution ; (iii) evaporation rate ; (iv) aircraft altitude and swath characteristics ; (v) volume and amount pesticide applied ; (vi) atmospheric conditions (turbulent or stable). The parameters required to define the risk of impact upon the environment include the following: (i) sensitive areas/species (location and type) ; (ii) pesticide toxicities/safe exposure levels ; and (iii) pesticide persistence/degradation rate.

2-10. CASE STUDIES ON PESTICIDE SPRAY TRANSPORT

Gas liquid chromatography (GLC or GC) for ecosystem analysis at the nanogram level was developed first by Coulson et al., (1959) followed by other chromatographic-mass spectral methods that increased detection and quantifiable sensitivity followed. These methods are widely used to study the fate of pesticides introduced into the environment.

2-10.1 Methods to Measure Pesticide Spray Transport

In the past half-century, artificial targets such as cards, slides, and plastic sheets have been used as tools in evaluation of spray management. Data produced through these methods are often misleading (Uk, 1977). Wiesner (1984) describes deposit cards as lacking diagnostic capabilities for interpretation of pesticide spray results and providing no insight into the reasons for success, variability or failure of spray programs.

Impingement probability studies have been limited to deposition on artificial targets. Size-limited deposition means that these deposits have no

quantitative or overall analytical significance. Further such targets are usually placed in open areas and do not even mimic deposition on adjacent foliage.

Methods for analysis of spray transport in a foliage environment were developed by Himel et al., (1965) and Himel and Moore (1967). The quantitation of spray mass transfer in foliage systems is complex as well as time and labor intensive.

Spray droplets in target and non-target areas can be determined by size and number on insects and/or natural foliage. Analytical systems which have had extensive field study include the fluorescent particle spray droplet system, (Himel et al., 1965; Himel and Moore, 1967; Himel, 1969a, 1969b); the dry liquids system, (Barry et al., 1977; Barry and Ekblad, 1978); the reversibly soluble pigment system, (Uk, 1977; Lawson and Uk, 1979); the fluorescent dye system, (Barry and Ekblad, 1978; Wiesner, 1984); the fluorescent pigment system, (Joyce, and Beaumont, 1978); and the encapsulated droplet system (Himel, 1982; Sundaram, 1982; Villaveces, 1984).

2-10.2 Case Studies

Case studies cited below provide critical evidence for testing the validity of the turbuuuulence theory.

2-10.2.1 Scottish Forestry Service Case Study

This research compared delivery of LV (aqueous) sprays - 20 L ha^{-1} and ULV (non-aqueous) sprays - 1 L ha^{-1}. A Micronaire nozzle was used and provided a VMD of 120-160 μm. In the 1979 tests, wind speeds of 8 to 25 km h^{-1} (5-15 miles h^{-1}) were encountered. The high wind speeds caused operational

flying problems, but actual deposition on the trees was increased and drift was decreased. Analytical methodology included the use of fluorescent pigments and the fluorescent particle spray droplet tracer method (Joyce and Beaumont, 1978; Ruthven, 1978; Joyce et al., 1979).

2-10.2.2 Canada Case Study

Downwind transfer of fenitrothion spray was measured using tracer systems in conjunction with meteorological measurements. The VMD of the spray was 58 μm (evaporated basis). In this research, droplet deposition (by number) on balsam fir needles peaked at 10 μm. Of 5000 droplets analyzed on target needles, 90.4% (by number) were < 60 μm (Wiesner, 1984).

2-10.2.3 United States Case Study -1.

Tracer studies involved BT, carbaryl and trichlorfon sprays. More than 90% of the droplets (by number) found on needles were < 60 μm (Barry, 1984; Barry and Ekblad, 1978; Barry et al., 1977).

2-10.2.4 Canada-USA Case Study

The encapsulated droplet tracer system is a recently developed analytical system to identify deposition patterns. The method uses spray droplets that encapsulate during transit. The capsules deposit on foliage or other surfaces as spheres or hemispheres which can be identified, measured and counted. Research groups conducting these tests included Forest Pest Management Institute (Canada), Canadian Forestry Service, U.S. Forest Service (CANUSA PROGRAM), and University of Georgia. (Villaveces, 1984)

2-10.2.5 United States Case Study -2.

The first analytical study of mass transfer by sprays using the fluorescent particle spray droplet tracer method was conducted from 1965 to 1969 (Himel and Moore, 1967, 1969b). The tests, carried out in Montana (spruce-fir forest) and Georgia (cotton field), allowed comparison of foliage and habitat differences. The D_{max} was 365 μm for the forest and 800 μm for the cotton field. Spray droplets on insects killed by the sprays were analyzed. Of 101,000 droplets analyzed, 98% (by number) were < 30 μm in diameter. Delivery of spray droplets to the conifer forest insects was not different in kind from delivery to cotton insects. No spray droplets larger than 120 μm in diameter were found on insects killed by the spray.

2-10.3 Summary

Since 1965, several mass transport studies of pesticide spraying have been carried out in the United States, Canada, and Great Britain by different research groups. The data from these studies are mutually consistent even though they represent different methodologies, test protocols, and field conditions. They confirm that the delivery and impingement of pest management sprays is governed by principles of spray physics. Only spray droplets < 100 to 150 μm deliver pesticides into foliage environments; large droplets fall to peripheral foliage and the ground; and numbers of droplets, foliage density, impingement probability, and turbulence are also crucial factors. The spray application of insecticides, fungicides and herbicides involve fundamental spray management principles. Mitigation of drift is a problem in risk management because drift is a concomitant result of all spraying techniques. Drift is exacerbated by evaporation and by unfavorable application conditions.

Principles of spray physics are a basis for computer-aided spray models. It may take decades before sufficient analytical data become available for widespread acceptance of computer-aided spray models for general field use.

The analytical data collected in Tables 2-2 to 2-5 and Figure 2-4 represent major interdisciplinary research studies with sprays. Each represents application of analytical tracer systems and literally thousands of hours of field and analytical time. It is important that these data be collected, presented, and reviewed because they are a basis for change in spray technology. Change is important because the spray application of pesticides is a multibillion-pound source of pesticides in the environment. The immensity of the problem of change in this industry can be illustrated by a composite of typical observations relative to current practices: "Yes I know that large droplets cannot enter foliage, but I have to use large droplet sprays to fight drift." Analytical data are given below as Tables 2-2 to 2-5 and illustrated in Fig. 2-6. Case studies cited above also provide critical evidence for testing the validity of the turbulence theory.

2-11 MODELING PESTICIDE SPRAY APPLICATION

Over the last two decades, the federal government has spent considerable effort in developing computer-based spray drift models in which theoretical approaches are represented by either diffusion or ballistic models.

Diffusion models are based on the assumption that the primary mechanism which drive the motion and deposition of the aerial spray particles is the mixing and interchange resulting from the spatial variation of particle concentration. Diffusion is a one-way process in which the total particle ensemble tends toward a state of equilibrium because areas having denser

concentration with high particle interaction tend to become less dense.

Since diffusion models consider particle ensembles, they are particularly useful for describing both spray drift and the environmental impact of the spray drift. There are two principal types of diffusion models: (i) those resulting from the mathematical solution of the diffusion equation, the so-called Gaussian assumptions and (ii) those based upon finite difference of the behavior of the pesticide sprays. The latter is generally the more versatile because it permits more realism in incorporation of physical variables, for example, temperature gradients, humidity, wind, turbulence, and topography. The diffusion model is complex to operate but its benefits frequently justify the extra effort.

In the ballistic model, a spray droplet is considered as a moving spherical mass governed by Newton's laws of motion (force of gravity and air resistance). Averaging over the ensemble of particle size yields the overall time history and spatial distribution of the spray cloud. Ballistic models are used for studies of spray droplets having diameters > 100-150 μm.

Complete description of polydisperse spray clouds whose particle diameters range from hundreds down to a few micrometers requires a combination of the diffusion and ballistic modeling approaches. In these combined models the spray deposition is commonly modeled by ballistic assumptions while drift is commonly approached on the basis of diffusion analogies. Since ballistic type models are, in general, simpler to computerize, complex particle behavior, e.g. effects of aircraft vertices, droplet evaporation, changes in mass and concentration of the spray cloud and temperature gradients is most often handled by this analysis technique.

Current aerial spray models are available as follows:

2-11.1 FSCBG Model

The (Forestry Service, Cramer, Barry, Grim Model) is an extension of early work done for the U.S. Army's at the Dugway Proving Ground by Dumbauld et al., (1975) and carried on by the H.E. Cramer Company by Dumbauld et al., (1977). The FSCBG model is a line source model which incorporates aircraft wake settling, line source dispersion, droplet evaporation, and canopy penetration. Concentration, deposition, and dosage above and below a downwind forest canopy are calculated for multiple spray lines.

This model has been used for spray prediction in a variety of spray applications by the U. S. Forest Service, including in pine seed orchards in the southern U.S. and in spruce budworm spraying programs in Maine (Ekblad and Barry, 1984).

2-11.2 AGDISP Model

The AGricultural DISPersion (AGDISP) model was developed by Bilianin et al., (1981) for NASA Langley Research Center and USDA Forest Service. It is based on description of the motion of discrete droplets. Integral dynamic equations for calculating droplet trajectories are provided. The model includes the influence of the spray delivery system, wake turbulence, atmospheric turbulence, gravity, and evaporation. The model has been principally applied to large droplet sizes.

2-11.3 Picot Model

The Picot model for Forest Spray Dispersion and Deposition (Bask and Picot, 1984) employs a finite difference technique to solve the

diffusion-advection equation. Atmospheric turbulence, gravitational settling, droplet evaporation, atomizer type, foliage, and limited wake effects are explicitly considered.

2-11.4 EPAMS Model

The Environmental Prototype Automatic Meteorological System (EPAMS) model is based on the Dugway Proving Ground line source dispersion model (Dumbauld and Bjorkland, 1977). The model incorporates complex terrain wind field effects in a Gaussian instantaneous line source model. Mixing layer depths and wind velocity are estimated based on stable atmospheric assumptions. Dispersion is computed from the Gaussian assumptions. Evaporation and micrometeorological effects are ignored.

2-11.5 Reid and Crabbe Model

The Reid-Crabbe models (Crabbe et al., 1980abc) are finite difference gradient transfer simulation techniques that uses a Lagrangian Markov chain formulation. The models consider atmospheric turbulence, droplet evaporation, gravitational settling, and initial droplet-size spectrum.

2-11.6 FWG Model

The FWG (Frost and Huang, 1981) model accounts for aircraft wake parameters, spray nozzle exit parameters, and mean and statistical atmospheric properties including turbulence. A fourth-order Runge-Kutta scheme is used to solve the three differential equations of motion. An aircraft vortex wake model is currently being incorporated. Evaporation is not considered.

2-11.7 Bragg Model

The Bragg model (Bragg, 1981) incorporates aircraft vortex wake, droplet evaporation and propeller effects. The vortex path subroutine evaluates wing and helicopter blade surface potential flow and computes the spanwise location and strength of wing-tip vertices. Wake properties are computed based on a viscous wake model. Drift and deposition are computed from the interactions between the droplets and the wake.

2-11.8 Miller Model

The Miller Model (Miller, 1980) examines the dispersal of agricultural sprays from airplanes, helicopters and ground spray rigs. The model is two dimensional and neglects the micro-meteorology of the canopy and droplet evaporation. Nozzle exit size distribution functions are computed based on measured spray deposition pattern with a few simplifying assumptions concerning the distribution shape. The model is applicable to a narrow range of turbulence parameters.

2-11.9 Trayford and Welsh Model

The Trayford and Welsh model (1977) considers wing tip vortices, evaporation and propeller swirl and computes droplet trajectories. The model applicability is generally limited to the near field (a few wingspans from the flight line).

2-11.10 The Cranfield Model

The Cranfield Institute of Technology model (Bache, 1975; Bache and Sayer, 1975; Bache and Uk 1975) simulates the deposition from a cloud diffusing about its center of gravity transported with the mean wind. The model was originally developed for the evaluation of agricultural spraying and neglects canopy factors and droplet evaporation. When combined with the canopy models also developed at the Cranfield Institute of Technology, realistic estimates of droplet transport within canopies are developed.

2-11.11 Loats/AIPHS Model

This model developed by Loats Associates, Inc. is an extension of the Cranfield model (Loats and Lloyd, 1983). The model was developed to simulate the dispersion and deposition of insecticides and herbicides to agricultural crops. The model includes methods for accounting for the effects of droplet evaporation. It is available in several forms including versions that run on small handheld calculators.

2-12 RESEARCH NEEDS FOR IMPROVED SPRAY TECHNOLOGY

Well-engineered, efficient pesticide delivery systems are urgently needed. The spray application of pesticides has never developed beyond its empirical basis. Most of the spray methods used today are deeply entrenched and difficult to change. If change is to come to pesticide spray methods, it must be based on widely available analytical mass transfer data. Because all methods for analyzing the mass transfer are time and labor intensive, there is a need for automation of foliage deposit analysis to make wide ranging data available to field agriculturists. Analysis of foliage samples must be adapted

to digital video methods. Wide availability of automated methods and their data is a key step to implement new methodologies in spray transfer and pest management.

There is a critical need to test and evaluate existing or improved mathematical models so that computer directed field spray programs can be developed and made readily available. The available models need extensive field testing in conjunction with analytical systems to justify widespread adaptation to computer programs aimed at pesticide efficiency, optimized pest management and risk management of drift.

2-13 CONCLUSIONS

From the above discussion on spray physics we conclude that:

1. Delivery efficiency for pesticide sprays is size-limited. The ultimate question is whether investment in large droplets in sprays is economically sound and biologically relevant in treating foliage systems.

2. Present spray technology does not conform to underlying principles of spray physics, thus it needs to undergo major change in methods and hardware. That change will, however, be slow because present methods appear to be rational and are deeply rooted. Principles of spray physics are a valid basis for computerized spray models.

3. Most current pesticide spray methods are inefficient. New, delivery technology must be based on efficient delivery to the target.

4. Broad-spectrum, polydisperse pesticide sprays can be evaluated by division into two discrete size segments > 150 μm having a probabilities of impingement = 1. Sizes < 100-150 μm have an impingement probability < 1. This is a major factor in determining the bioefficacy of sprays.

5. A foliage barrier exists for spray droplets > 100-150 μm. They are filtered out in the first few millimeters of foliage.

6. Most insects and disease vectors live within a protective microhabitat. Effective management requires delivery of the pest control agent into and on that microhabitat.

7. Mass and droplet transfer in herbicide sprays has never been quantified.

8. Spray drift is the overriding factor in the use of herbicides. Control of spray drift using ultra-large, polydisperse sprays is not an ultimate solution.

9. Most pesticides are subject to volatilization from sprays, from foliage and from the ground. This is an environmental management problem whose significance has not been properly evaluated.

10. Efficient pesticide delivery systems must be developed.

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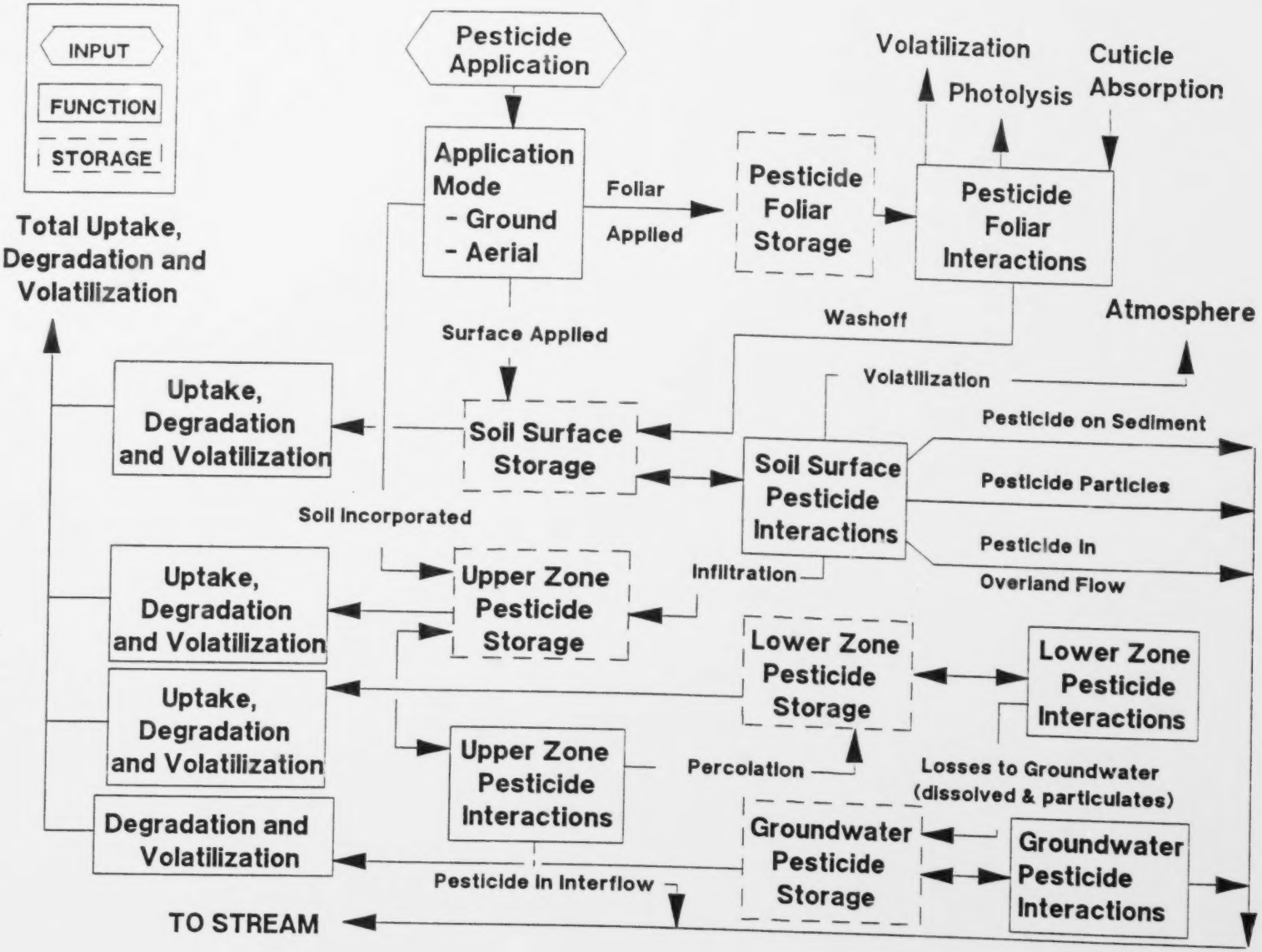

Figure 2-1. Pesticide transport and transformation in the soil-plant environment and vadose zone (After Donigian and Crawford, 1976).

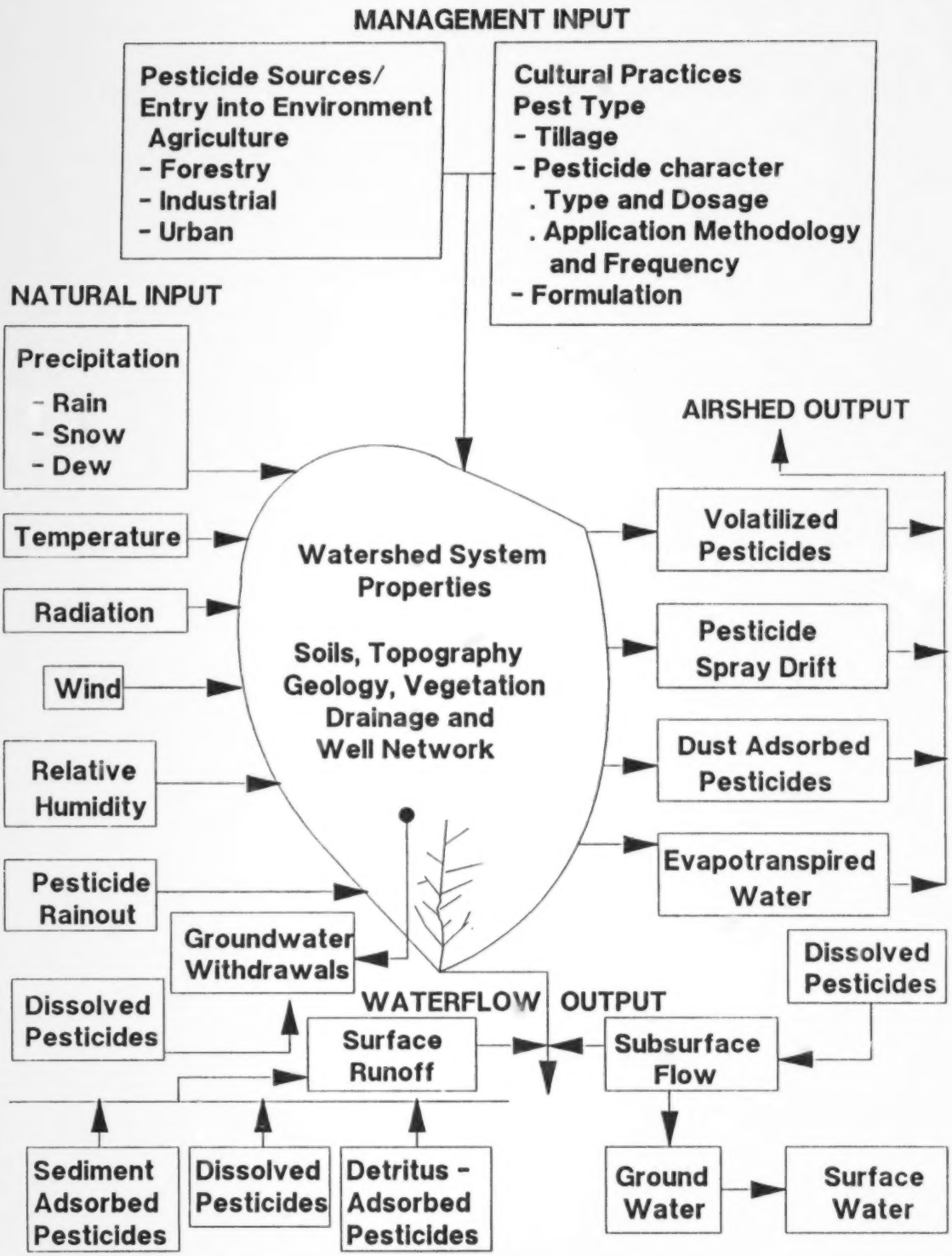

Figure 2-2. Factors influencing the behaviour and export of pesticides from a watershed (After Bailey et al., 1985).

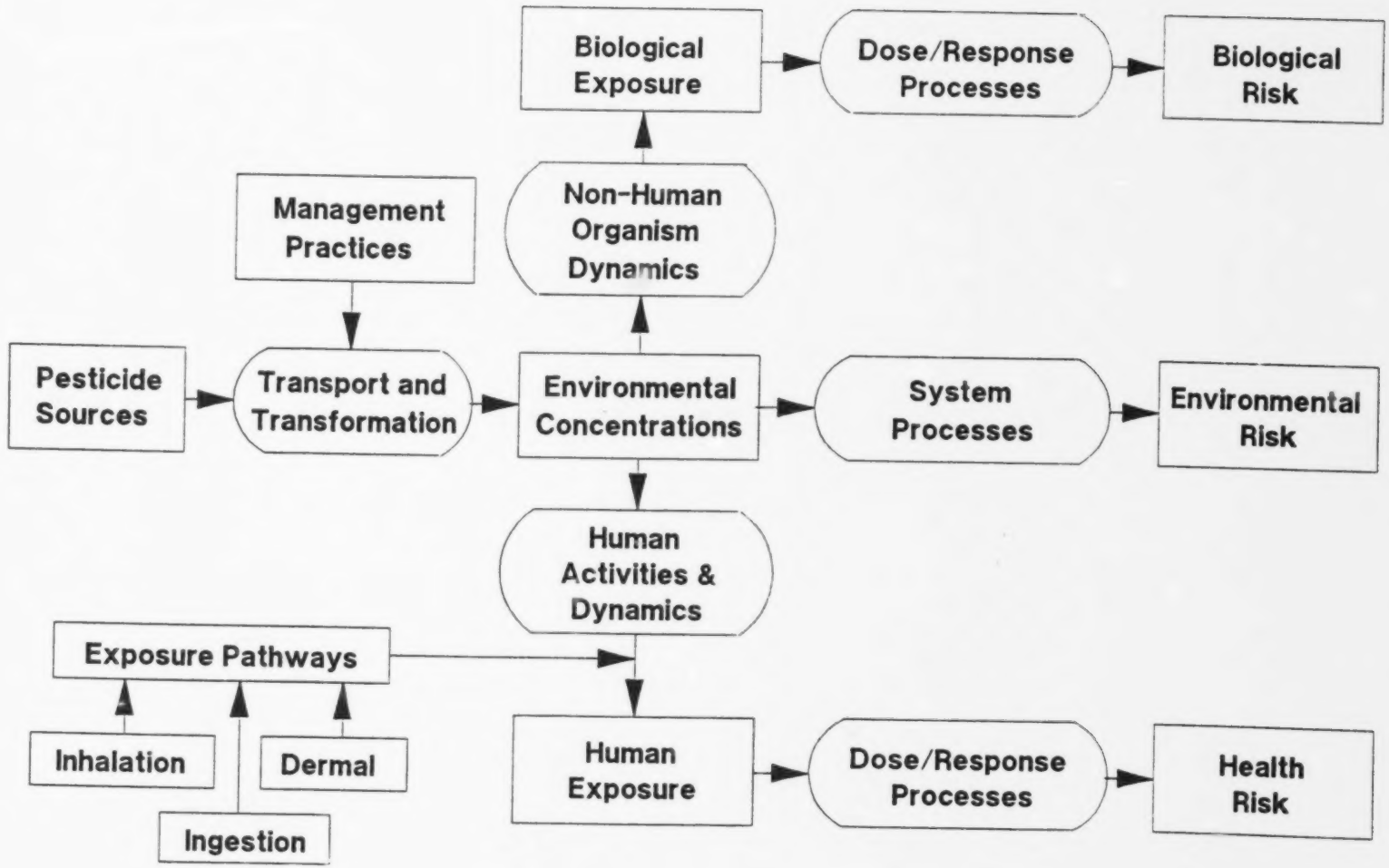

Figure 2-3. Concept of pesticide exposure and risk assessment.

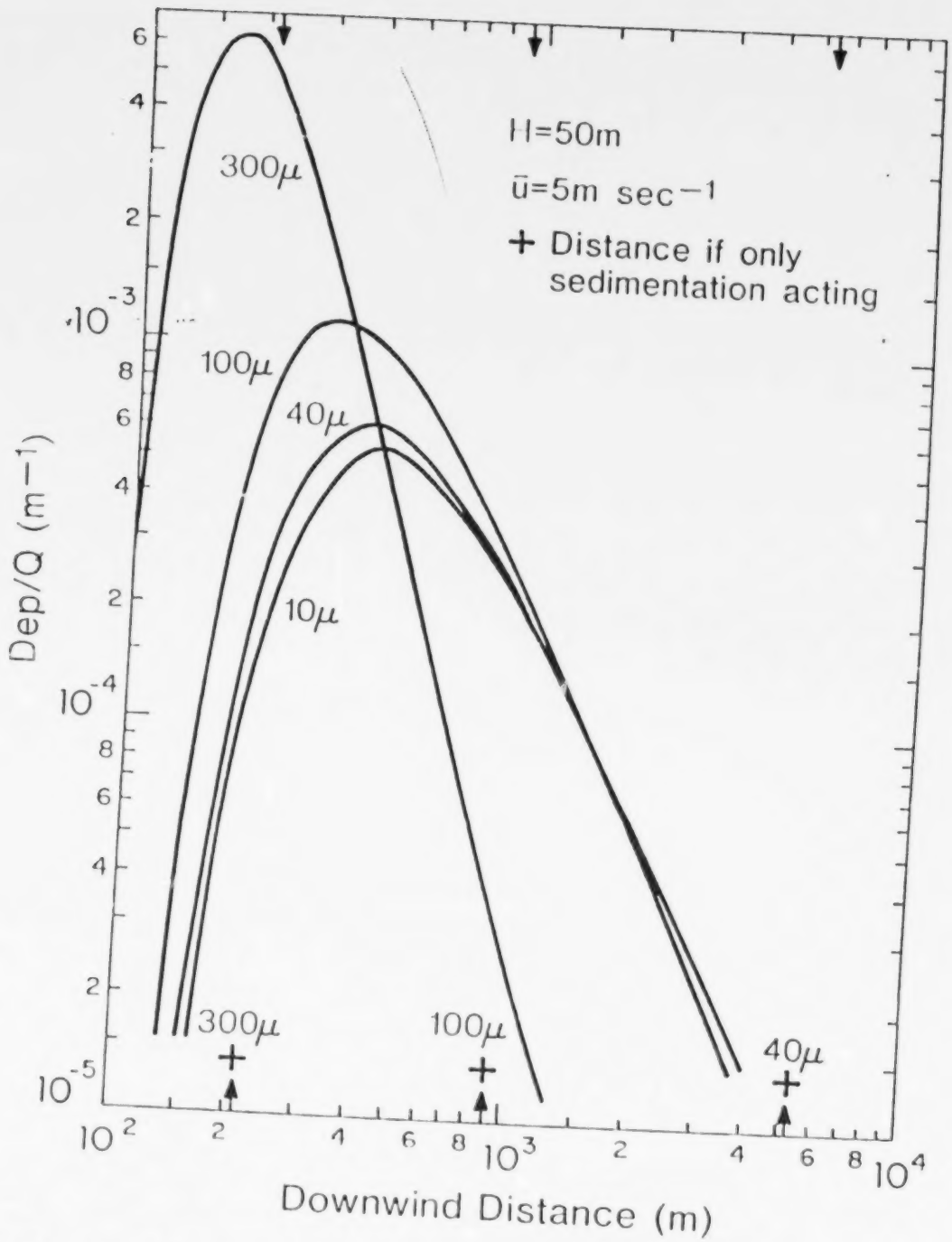

Figure 2-4. Calculated transport of pesticide spray (After Cramer and Boyle, 1976).

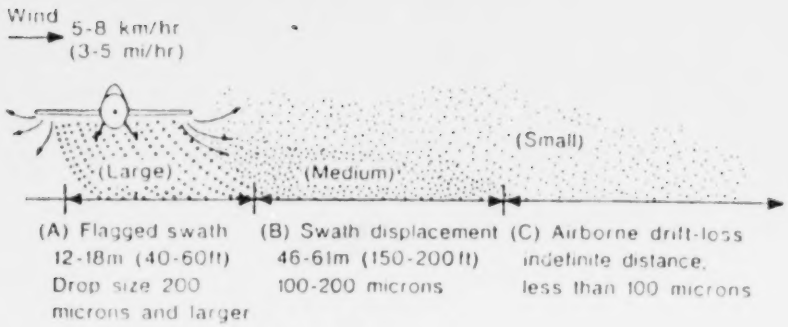

Figure 2-5. Drift calculated by sedimentation theory. Reproduced from Akesson and Yates, 1984. Reprinted with permission from ACS Symposium Series, 238, Copyright, 1984.

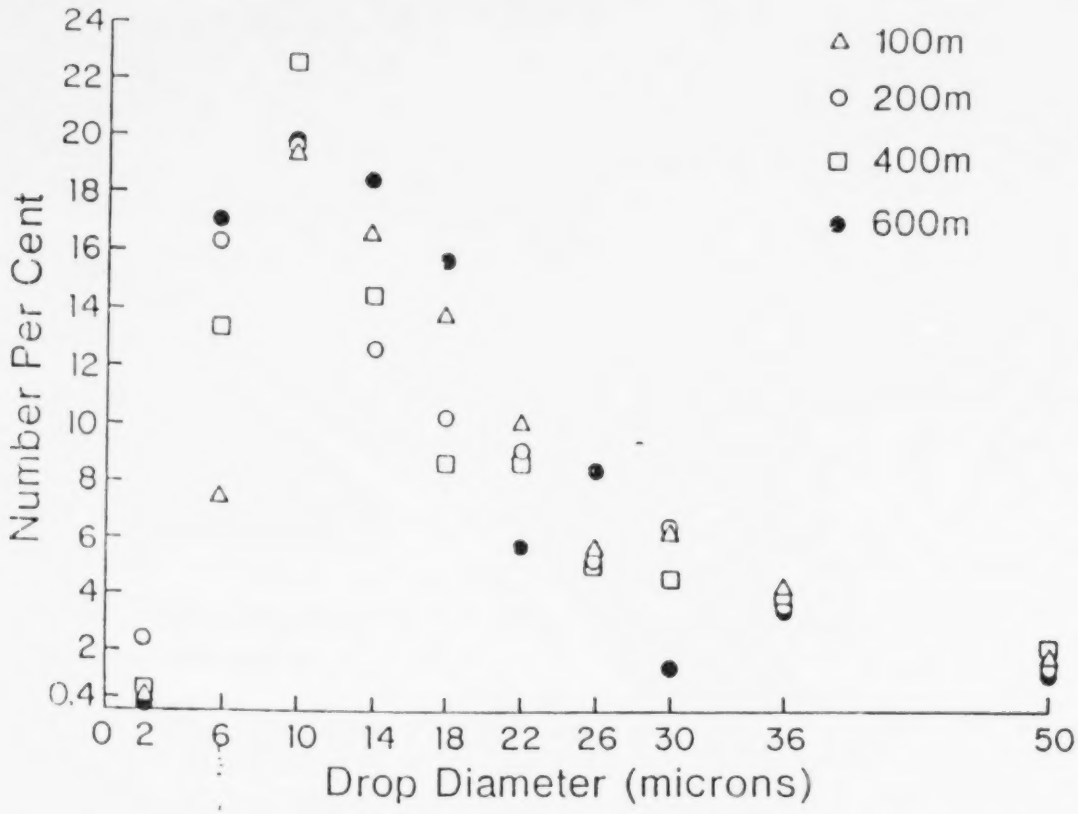

Figure 2-6. Droplet spectra deposited on balsam fir needles under unstable conditions - 100, 200, 400 and 600 meters from the swath. Reproduced from Wiesner, 1984. Reprinted with permission from ACS Symposium Series, 238, Copyright, 1984.

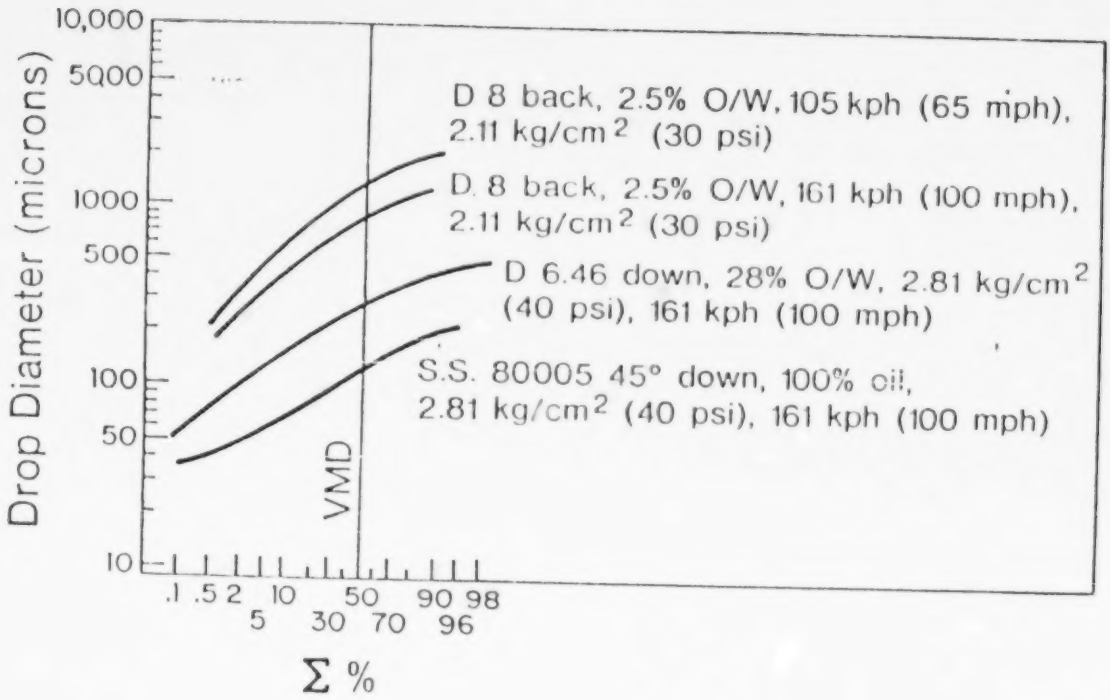

Figure 2-7. Log normal distribution of drop diameters.

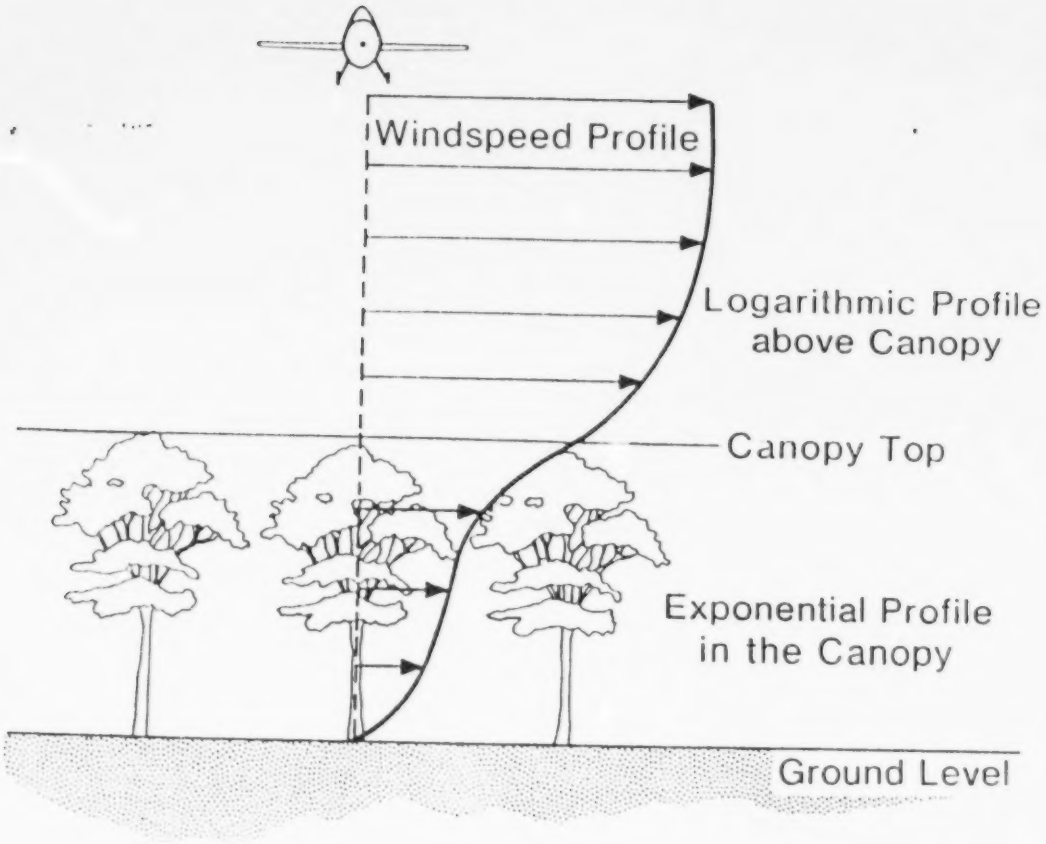

Figure 2-8. Forest canopy influence on windspeed profile.

Table 2-1 **Pesticide Sources and Environmental Exposure Pathways.**

Pesticide Source	Transport Process	Exposure Pathway	Receptor (Population at risk)
canopy	volatilization	inhalation skin contact	human animals
crop residue	volatilization	inhalation/ skin contact	human animals
soil surface	volatilization	inhalation/ skin contact	human animals
root zone and below	volatilization	inhalation/ skin contact	human animals
grain/foilage	manufacturing /feeding*	food/ingestion	human animals
crop residue	overland flow*	surface water (potable water)/ ingestion	human fish
runnoff	overland flow*	surface water (potable water and food chain)	human fish
eroded soil particles and formulation - bound	overland flow*	ingestion surface water (food chain)/ ingestion, contact	fish
leachate -dissolved -bound on colloidal particles	leaching/ percolation*	groundwater (potable water)/ ingestion	human animals

* Environmental flux of concern to either on-site or off-site receptors. After Bailey et al., 1985.

Table 2-2 **Comparison of LV and ULV sprays in Pine Beauty Moth Control in Scotland, 1978.**

	LV*	ULV
mean deposit (μg/20 needles)	23.6	41.2
mean deposit (μg/single bud)	17.5	18.8
mean deposit (μg/larvae)	4.4	22.4
lost outside target area (%)	20	1
lost to ground (%)	38	5
collected by target surfaces (%)	42	94
average size of droplet on needles	50 μm	50 μm
maximum size droplet on needles	~120 μm	~120 μm
90 % of droplets found on ground	>150 μm	>150 μm

* Both LV and ULV sprays were produced by a Micronaire nozzle under conditions to optimize the spray spectra available from the nozzle (VMP 120 - 160 μm). Pigment and the fluoresent particle spray droplet tracer methods were used (After Joyce and Beaumont, 1978; Ruthven, 1978; and Joyce et al., 1979.).

Table 2-3 **Number of Droplets Observed on Conifer Needles by Size Categories in a U.S. Forest Service Field Trial, 1975 with Three Different Pesticides*.**

Drop Size range (μm)	Pesticide Type: Bt[1] #	Bt[1] cum.%	Carbaryl #	Carbaryl cum.%	Trichlorfon #	Trichlorfon cum.%
< 4	108	16	137	11	353	19
4-10	239	51	236	31	323	36
10-15	139	71	106	40	200	47
15-21	28	75	139	51	228	59
21-31	90	89	254	73	338	77
31-41	10	90	76	79	116	83
41-61	24	94	88	86	57	86
61-81	25	97	73	92	108	92
81-121	7	98	45	96	87	97
121-151	8	99	26	98	21	98
151-200	1	99	17	99	24	99
> 200	2	100	5	100	18	100

* (After Barry, 1984; Barry and Ekblad, 1978; Barry et al., 1978)

1. Bacillus thuringiensis

Table 2-4 **Encapsulated Droplets on Conifer Needles in a Canadian - U.S. Field Trial, 1982 - 1983*.**

Drop size μm	Average Size, μm	Number %	Cum. %	Volume %	Cum.%
2-5	3	3	3	0	0.0
6-10	8	14	17	0.3	0.3
11-20	15	47	64	7.8	8.14
21-30	25	24	88	24	31.6
31-40	35	8	96	24.5	56.1
41-50	45	2.3	98	13.8	70
51-75	63	0.9	99	9	79
76-100	88	0.7	99.8	15.5	94
101-125	100	0.1	100	5.9	100

* (after Crabbe et al., 1980 a, b, c.)

Table 2-5 **Insecticide Spray Droplet Distribution on Four Insects from Five Different Field Studies*.**

	Droplet Size Range (μm)					
	21-30	31-40	41-50	51-60	61-120	>120
	Droplet Percent					
Spruce budworm[1]	92	3.5	1.7	1.4	---	---
Boll weevil[2]	97	2	0.4	---	---	---
Boll worm[3]	98	1.3	0.2	---	---	---
Cabbage looper[4]	97	1.9	0.6	---	---	---

* (After Himel and Moore, 1967, 1969) Fluorescent particle tracer system used.

1. Choristoneura fumiferana
2. Anthonomus grandis
3. Helothis zea
4. Trichoplusia ni

Table 2-6 **Major Components of Pesticides Losses in Spray Processes.**

1. Delivery losses (60 - 80 % of most sprays)
   a. Directly to the soil
   b. Peripheral foliage
2. Primary volatilization losses to the air
   (3 - 10 % of many sprays, but depends on volatility)
3. Primary particulate drift losses (in the air)
   (3 - 5 % of many sprays)

Table 2-7 **Terminal Velocity of Spheres (in Still Air) (Reynolds number < 0.1)*.**

Droplet Diameter μm	Fall Rate, (sp.gr - 1) m sec^{-1}
1	0.00003
10	0.003
20	0.012
50	0.075
100	0.275
200	0.721
500	2.139

* after Himel (1982)